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LASER SPECTROSCOPIC INVESTIGATIONS OF ORGANIC ALKOXY AND PEROXY RADICALS

By

Md Asmaul Reza

A Dissertation

Submitted to the Faculty of the

College of Arts and Sciences of the University of Louisville

in Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy in Chemistry

Department of Chemistry

University of Louisville

Louisville, Kentucky

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LASER SPECTROSCOPIC INVESTIGATIONS OF ORGANIC ALKOXY AND PEROXY RADICALS

Md Asmaul Reza

A Dissertation Approved on

October 31, 2019

by the following Dissertation Committee:

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This dissertation is dedicated to my parents and my lovely wife

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ABSTRACT

LASER SPECTROSCOPIC INVESTIGATIONS OF ORGANIC ALKOXY AND PEROXY RADICALS

Md Asmaul Reza

October 31, 2019

Understanding the mechanism of combustion reactions is key for advancing internal combustion engine design, improving the efficiency of ignition chemical reactions, and reducing pollutant formation. In order to model the extremely complicated chemical kinetics of combustion processes, it is critical to detect and identify transient reactive chemical intermediates, particularly free radicals. Hence, it needs to be fully understood the gas-phase chemistry of organic compounds in the lower atmosphere. Over the past fifty years, parallel advancement in observational, experimental, and theoretical techniques, tremendous strides have been made in our understanding of the role of organic compounds in the atmosphere. Combustion chemistry is extremely complex, partly because of the large number of reaction intermediates that are involved in the process. Here we propose laser spectroscopic investigations of oxygen-containing combustion intermediates such as alkoxy ($\text{RO}\cdot$) and peroxy ($\text{ROO}\cdot$) radicals. These investigations are aimed at elucidating

the structures and dynamics of free radicals, which are generated by laser photolysis of judiciously chosen precursors in a flow cell and supersonic jet expansion.

Spectroscopic interrogation of these species will be carried out using laser-induced fluorescence (LIF) spectroscopy, disperse fluorescence (DF), and cavity ring-down (CRD) spectroscopy. Vibrational structure of excited electronic states has been recorded using LIF and UV/visible/near-IR CRDS techniques, whereas DF and mid-IR CRDS techniques can be used to explore the vibrational structure of ground electronic states. Vibronic analyses were performed for the experimental spectra with the aid of quantum calculations. Accurate transition origin frequencies, excited and ground state vibrational frequencies, and Frank-Condon factors were determined for different intermediates such as isobutoxy, 2-methyl-1-butoxy, isopentoxy, 1-,2-,3-, and 4-methylcyclohexoxy, and 1-,2-, and 3-methyl allyl peroxy.

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CHAPTER I

INTRODUCTION

Laser spectroscopy is a powerful tool for the identification and diagnosis of chemical reaction intermediates. It has been arguably the pre-eminent tool for the study of molecular dynamics and chemical kinetics, which has greatly advanced our understanding of the electronic structure and chemical reactivity. However, there still exist vast, unexplored gaps in our knowledge that demand further investigation. A major experimental challenge for the molecular spectroscopist is the generation of target molecular species in sufficient quantities and under the appropriate conditions to permit their detailed study by high-resolution methods. Particularly difficult are reactive species, mostly free radicals and molecular complexes. Different transient species can be involved in chemical reactions as intermediates. Spectroscopic identification of the intermediates provides information about their structural as well as dynamical properties, which can be useful in quantifying the fate of different species involved in the chemical reaction. Due to their transient nature and presence of unpaired electrons, obtaining spectroscopic information of these important species has been an experimental as well as a theoretical challenge. The advancement in experimental techniques to isolate these species, laser technology, and quantum chemistry

calculations have made it possible to obtain spectroscopic identification of transient species in recent times. These reactions affect atmospheric and combustion chemistry, both of which affect almost every aspect of life on earth. Various intermediates, like alkyl alkoxy and peroxy radicals, are involved in these chemical reactions.

1.1 Alkoxy Radicals

Alkoxy radicals ($\text{RO}\cdot$) are important reaction intermediates in the combustion of fossil fuels and the atmosphere, especially in the troposphere.¹⁻³ Spectroscopic study of the free radicals namely substituted and unsaturated alkoxy and peroxy radicals can advance our understanding of many important chemical processes, including combustion of fossil fuels and biofuels in internal combustion engines, and oxidation of hydrocarbons in the atmosphere and interstellar space.³⁻⁵ The oxidation of hydrocarbon is among the most important chemical processes. In these oxidative processes, alkoxy radicals are often a crucial intermediate that can react further via one of several mechanisms. The chemistry of the alkoxy radicals has been well investigated.⁶⁻⁸ Figure 1.1⁸ shows the reaction mechanism in hydrocarbon combustion at low-temperature between about 500 and 1000 K. Alkoxy radicals are formed by branching reaction. The oxidation of hydrocarbon is initiated by hydroxyl (OH) radicals and formed peroxy radicals that can react and decompose to produce alkoxy radicals. Also, in the presence of NO_x , alkoxy radicals are formed from alkanes in the troposphere predominantly by the following mechanism:

The reactions of the simplest oxygen-containing hydrocarbon, e.g., alkoxy ($\text{RO}\cdot$) and peroxy ($\text{ROO}\cdot$) radicals are of considerable interest in atmospheric chemistry.^{1, 9} Recently open-chain alkoxy radicals- methoxy ($\text{CH}_3\text{O}\cdot$),¹⁰⁻²⁰ ethoxy ($\text{C}_2\text{H}_5\text{O}\cdot$),^{10, 21-24} and isopropoxy ($\text{C}_3\text{H}_7\text{O}\cdot$)²⁵⁻²⁷ have been studied extensively, and their spectroscopic information has become available. While the smaller alkoxy radicals have drawn significant attention, the spectroscopic study of larger alkoxy radicals is much sparser. It was generally felt that the fluorescence quantum yield for the $\tilde{B}-\tilde{X}$ transition would rapidly decrease as non-radiative decay processes became dominant in the larger alkoxy radicals. That perception began to change when LIF spectra of iso-butoxy, 2-methyl -1-butoxy, isopentoxy *t*-pentoxy, 3-pentoxy, *t*-butoxy, and 2-butoxy were observed at near ambient temperature.²⁸⁻³¹

The reactions of alkoxy radicals in the atmosphere are significant and hence of great interest. The most important reactions are decomposition, reaction with O_2 and isomerization.¹ Among many alkoxy radicals we have studied, isobutoxy, 2-methyl -1-butoxy, and isopentoxy are especially interesting in dynamics studies because of its β C-C bond scission. Most alkoxy radicals have multiple structural and conformational isomers. It is well-known that the rate constants of alkoxy reactions can be highly sensitive to their conformations in the ground and excited states. For instance, the energy barrier for the isomerization of ground-state 1-butoxy (a 1,5 H-shift) is 3.6 kcal/mol lower than decomposition, whereas the barrier of isobutoxy isomerization (a 1,4 H-shift) is 10.6

kcal/mol higher than that of decomposition.²⁹ This is due to the fact that the isomerization of isobutoxy occurs via a six-membered transition state, while the transition state of 1-butoxy isomerization contains a five-membered ring that has higher strain energy and is less stable. Eventual stable products of particular hydrocarbon oxidation are determined by the competition between various potential reaction pathways of alkoxy radicals.

Cyclic-alkoxy radicals are another important reaction intermediates that still remain unexplored despite those play significance roles in combustion fuels and the atmosphere. For example, the cyclohexoxy radical is a key intermediate in the oxidation of cyclohexane, which is an important constituent of automobile fuel. Among cyclic-alkoxy radicals, the cyclohexoxy radicals and its substituted derivatives like methylcyclohexoxy (MCHO) are of special interest due to their particular stability of the six-membered ring structure and complicated conformational behavior.³² In addition, the cyclohexoxy radical, as well as other cyclic alkoxy radicals, is a prototypical pseudo-Jahn-Teller (pJT) molecule. Analysis of the vibronic structures of MCHO radicals helps to understand the coupling between close-lying potential energy surfaces (PESs), including pJT and spin-orbit (SO) splitting.^{24,}
³³ The lowest three electronic states $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ of alkoxy radicals are well defined in the literature.^{26, 32, 34, 35} Its two lowest electronic states can be separated by as low as 61 cm⁻¹. Essentially all alkoxy radicals can be treated as the alkyl substitution of the methoxy radicals (CH₃O), which has C_{3v} symmetry and is orbitally doubly degenerate. In the primary, secondary and tertiary alkoxy radicals such as ethoxy, cyclohexoxy and MCHO, the alkyl substitution reduces the molecular symmetry from C_{3v} to C_s / C_I and removes the orbital degeneracy. The $\tilde{X}$ ²E state of the methoxy radical therefore splits into two close-lying states ($\tilde{X}$ and $\tilde{A}$) with A' and A'' symmetry, which have the half-filled orbital of the

oxygen-atom within the C_s plane (p_x) and perpendicular to it (p_y). the different alkyl groups interact differently with the p_x and p_y orbitals, which results in different $\tilde{A}-\tilde{X}$ energy separation between the lowest vibrational levels of these two states. The mechanism of interaction between these two close-lying states is of significant theoretical interest. Chemical kinetics and intramolecular dynamics of MCHOs, including alkoxy radicals, in general, are also affected by these lowest-energy electronic states ($\tilde{X}$ and $\tilde{A}$).

Conformation-specific studies of alkoxy radicals, especially that of the correlation between their structures and their reactivities, are, therefore, of significant importance to atmospheric chemistry. The dispersed fluorescence (DF) spectra of alkoxy radicals, which elucidate the energy level structure of lower electronic states of the free radical. It is therefore of interest to obtain the DF spectra of isobutoxy and make a comparison with the other three isomers. The DF spectra of alkoxy radicals can also be used to test the conformational assignment of the laser-induced fluorescence (LIF) spectrum previously reported.

This situation began to change recently with reports of the laser-induced fluorescence (LIF) spectrum of iso-butoxy, 2-methyl -1-butoxy and isopentoxy by Liang *et al.*²⁹ The observed LIF spectra for the electronic transition from $\tilde{B} \leftarrow \tilde{X}$ state corresponds to the promotion of one electron from σ orbital of the C-O bond to the half-filled non-bonding orbital of the O atom. However, they were failure to reported conformational assignments by using their structured LIF spectra of iso-butoxy and 2-methyl-1-butoxy. Furthermore, they did not assign their reported LIF spectrum of isopentoxy radicals. Also, Lin *et al.*³⁶ and Wu *et al.*³⁷ reported the first observation of jet-cooled LIF excitation spectra of all four MCHO isomer. Their spectra stimulated us to try to obtain simpler, jet-

cooled LIF and DF spectra of these species. Such spectra can give us valuable information on the photo-physical and dynamical properties of these radicals.

We have studied the vibrational structure of the isopentoxy by jet-cooled LIF spectroscopy. Also, we have studied the vibrational structures of the isobutoxy, 2-methyl-1-butoxy, isopentoxy, and MCHOs by jet-cooled DF spectroscopy. The recorded spectrum has been analyzed and assigned on the basis of vibrational frequencies and Franck-Condon factors (FCF) predicted by quantum chemical calculations. The intensity pattern and spectral distribution of the vibronic transition in the DF spectra depend on geometry and symmetry of $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ -states.

1.2 Peroxy Radicals

Understanding the mechanism of combustion reactions is critical for advancing internal combustion engine design, improving the efficiency of ignition chemical reactions, and reducing pollutant formation. In order to model the extremely complicated chemical kinetics of combustion processes,^{3, 38} it is critical to detect and identify transient reactive chemical intermediates, particularly free radicals. Many intermediates in fossil fuel combustion, however, remain elusive or unidentified. Peroxy radicals ($\text{ROO}^\cdot$) are the single most important reaction intermediates in low-temperature combustion because they initiate the chain reactions.^{39, 40} In low-temperature combustion (<700 K), the mechanism of peroxy radical formation begins with the abstraction of a hydrogen atom from the hydrocarbon fuel (RH) by a hydroxyl radical (OH) to form an alkyl radical ($\text{R}^\cdot$). The alkyl

radical undergoes a 3-body reaction with molecular oxygen to form an alkyl peroxy radicals ($\text{RO}_2^\cdot$).^{9, 39-42}

Once the peroxy radical is formed, the reaction can branch in several ways, as shown in Figure 1.1.⁸ HO_2 can react with it yielding an alkyl hydroperoxide which can decompose into an alkoxy radical and OH, or the peroxy radical can eliminate HO_2 directly to give an alkene. The isomerization of peroxy radicals leads to the formation of QOOH species. The rate of QOOH formation is governed by how large the ring structure intermediate and the type of the hydrogen atoms present (primary, secondary, tertiary). The formation of the QOOH species can lead to a chain branching step in which two additional OH radicals are formed along with an oxy radical.

Eventually, this will lead to an explosive increase in radical concentration, oxidation rate, and temperature to give autoignition, or “engine knocking,” which is an uncontrolled burn of the hydrocarbon fuel and the limiting factor in the thermodynamic efficiency of the engine. In order to decrease engine knock the molecular structure of the fuel must be considered with regard to preventing the peroxy radical isomerization to QOOH.⁴³⁻⁴⁸ When more branched hydrocarbons are used in the fuel, hydrogen atom

transfer will have to proceed through three and four-membered rings, which have high ring strain and will prevent the formation of QOOH.

Peroxy radical chemistry is also important in the atmospheric oxidation of volatile organic compounds (VOCs), such as alkanes. It is well known that their chemistry plays a key role in the atmosphere for the formation of ozone (O₃), secondary organic aerosol (SOA), and other secondary pollutants.^{39, 49-51} Approximately 1300 Tg of hydrocarbons are emitted each year into the atmosphere from biogenic and anthropogenic sources.⁵² The oxidation of hydrocarbons in the atmosphere are initiated by OH or Cl[•], which are also present in the atmosphere and formed alkyl radicals.⁵³ The alkyl radical then reacts rapidly with molecular oxygen in the presence of a third body (M, M-typically N₂), which stabilizes the peroxy radical product by collision. The peroxy radicals are involved in an important reaction cycle of ozone production in the atmosphere, particularly in the troposphere. For example, O₃ can be produced in the troposphere, where it is considered a pollutant, via peroxy radicals' reaction with NO:

Peroxy radicals reaction with NO produces excess amounts of NO₂ in the troposphere, where it can be photolyzed by sunlight to generate oxygen atoms. The oxygen atoms then react with molecular oxygen to produce tropospheric O₃^{41, 54} which, is

considered a health hazard. The second reaction of peroxy radicals with NO in the troposphere can produce excess amounts of hydroxyl radical:

The OH radicals can then migrate from the troposphere to the stratosphere, where O₃ is considered a filter against UV radiation, and reduce the amount of O₃ present putting our health at risk.⁵⁵

In addition to the atmospheric oxidation of alkanes by OH and Cl radicals, large quantities of alkenes emitted into the atmosphere are readily oxidized by them as well and undergo reactions that can pollute the troposphere.^{54, 56-58} The double bond of an alkene can be attacked by OH to give a hydroxy alkyl radical that can react with molecular oxygen in a three-body reaction to yield hydroxyperoxy radicals.⁵⁹⁻⁶⁵ Allyl group-containing peroxy radicals are particularly important because they are generated in significant quantities by the OH-initiated oxidation of isoprene, the most reactive and most abundant non-methane biogenic hydrocarbon.⁶⁶⁻⁶⁹ It has been shown in Figure 1.2⁷² that there are four of the six possible isomeric peroxies formed in the early stages of isoprene oxidation.⁷⁰⁻⁷²

The atmospheric oxidation of methyl allyl can also serve as a prototype for larger alkenes, such as isoprene and other unsaturated hydrocarbons, which are emitted in even

higher quantities. After methane (emission rates of ~ 600 Tg/yr),⁵² isoprene is the most abundant hydrocarbon emitted into the atmosphere with global emission rates reaching between 450-500 Tg/yr and an atmospheric concentration between 1-30 ppb.^{52, 73, 74} As with other alkenes isoprene has a very high reactivity towards OH radical which adds across a double bond followed by reaction of the resulting radical with molecular oxygen. This is combined with the high concentration of isoprene in the atmosphere makes the OH/O₂+isoprene reaction a critical atmospheric process, and it has been the subject of many theoretical and experimental studies.^{60-62, 65, 70, 75-81}

For many years the best way to spectroscopically observe peroxy radicals was to probe their $\tilde{B} \leftarrow \tilde{X}$ absorption located in the UV region. However, there is a considerable disadvantage to using this transition to distinguish among different peroxy radicals. The $\tilde{B} \leftarrow \tilde{X}$ transition generally involves the promotion of an electron from the second-highest occupied molecular orbital (HOMO-1) to the singly occupied molecular orbital (SOMO). Hence, the $\tilde{B} \leftarrow \tilde{X}$ transition involves the promotion of an electron from a bonding orbital to an antibonding orbital so that when a peroxy radical undergoes a transition to the state, the O-O bond dissociates⁸² (Figure 1.3). This gives rise to a repulsive $\tilde{B}$ -state potential energy surface, and the resulting spectrum for all peroxy radicals is a broad featureless absorption near 240 nm. This lack of any observable structure makes the UV transition a poor diagnostic with which to identify different peroxy radicals. Alternatively, the $\tilde{A} \leftarrow \tilde{X}$ transition of peroxy radicals is located in the near-IR and is a HOMO to SOMO transition. The HOMO of peroxy radicals is nonbonding along the OO bond $\tilde{A} \leftarrow \tilde{X}$ making the transition a promotion of an electron from a nonbonding to antibonding orbital. Therefore, the $\tilde{A}$ -state is a bound state, and upon excitation, to the $\tilde{A}$ -state, there is only a lengthening

of the O-O bond instead of complete dissociation. These qualities indicate that the $\tilde{A} \leftarrow \tilde{X}$ spectra of peroxy radicals will be structured and characteristic of a given RO₂ radical. This allows the differentiation among different peroxy radicals and makes the $\tilde{A} \leftarrow \tilde{X}$ transition an excellent diagnostic with which to observe peroxy radicals. However, observing the $\tilde{A} \leftarrow \tilde{X}$ transition may be experimentally difficult as it is based on the highly forbidden $a^1\Delta_g - \tilde{X}^3\Sigma_g^-$ transition of the O₂ chromophore.⁸³ Consequently, the cross section for this transition is $\approx 10^4$ times smaller than the $\tilde{B} \leftarrow \tilde{X}$ transition. Unfortunately, traditional absorption experiments do not have the sensitivity to detect this weak transition. However, the CRDS technique can be used to overcome the obstacle of studying a trace gas species with a weak transition.

Laser spectroscopy is a powerful tool for identification and diagnostics of chemical reaction intermediates; hence, it is of great importance to energy research. Different experimental methods were used for the efficient detection of the alkoxy and peroxy intermediates. LIF and DF techniques were used to identify different electronic states. LIF and DF are a sensitive background free technique for probing fluorescing species. DF spectra for the $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ transitions of isobutoxy and 2-methyl-1-butoxy are presented in Chapter (IV). LIF and DF spectra for the $\tilde{B} \leftarrow \tilde{X}$, $\tilde{B} \rightarrow \tilde{X}$, and $\tilde{B} \rightarrow \tilde{A}$ transitions of isopentoxo is presented in the Chapter (V). In Chapters VI and VII, DF spectra for the $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ transitions of 1-, 2-, 3-, and 4-MCHO are discussed. Quantum chemical calculations have been carried out to assist the identification of the spectral carriers and simulation of experimentally obtained spectra, from which molecular parameters such as electronic transition energies and vibrational frequencies of both electronic states can be determined. These parameters, in return, can be used to benchmark the calculations.

Notwithstanding the achievements, the capability of the current LIF/DF apparatus is limited by the nature of the spectroscopic techniques and the laser sources available. In order to gain a better understanding of the free radicals currently being studied in our lab and to include more combustion intermediates into future spectroscopic investigations, these limitations need to be overcome by employing new spectroscopic techniques and radiation sources. Cavity ring-down spectroscopy (CRDS), being an absorption technique with high sensitivity, is an ideal option. Because most molecules have absorptions due to electronic transitions in the UV/visible region, even when the excited state is radiationless, the absorption-based CRDS technique is more versatile than LIF/DF technique. Near-IR CRDS spectrum for the $\tilde{A}-\tilde{X}$ transition methyl allyl peroxy radical is presented in Chapter VIII.

Figure 1.1. Schematic diagram for combustion of hydrocarbons taken from ref. [8].

Fig. 1.2. Mechanism of peroxy radical formation from OH-initiated oxidation of isoprene. The allyl peroxy functionality (highlighted in red) is achieved in four of the six possible addition sequences taken from ref. [72].

Figure 1.3. Methyl peroxy potential energy surfaces of the $\tilde{X}$, $\tilde{A}$ and $\tilde{B}$ -states as a function of R_{OO} taken from ref. [83].

CHAPTER II

EXPERIMENTAL METHODS

2.1 Laser-Induced Fluorescence (LIF) and Dispersed Fluorescence (DF) Spectroscopy

Laser-induced fluorescence (LIF) and Dispersed Fluorescence (DF) technique coupled with supersonic jet expansion have been used to study the $\tilde{B} \leftrightarrow \tilde{X}$ transition of various primary,^{15, 28, 84, 85} secondary,^{28, 84} tertiary,⁸⁴ and unsaturated^{86, 87} alkoxy radicals. Moderate-resolution, as well as high-resolution spectra, have been obtained and analyzed to give accurate transition energies, vibrational frequencies, and rotational/spin-rotational constants.^{88, 89} It was therefore reasonable to try to obtain similar LIF, and DF characterization of isobutoxy, 2-methyl-1-butoxy, isopentoxy and methyl substituted cyclohexoxy radicals.

2.1.1 Introduction

LIF and DF spectroscopy was used to obtain spectra of fluorescing radicals and stable species. In LIF spectroscopy, fluorescence emitted by a sample is collected as a function of the probing laser wavelength. Depending on the electronic structure of a sample, it can absorb laser radiation at specific wavelengths. Following absorption, the newly populated

excited states can decay back to the ground state through fluorescence. Fluorescence from the sample is collected through a lens system perpendicular to the probing radiation and focused on a photomultiplier (PMT) tube. The collection of fluorescence perpendicular to the direction of the laser radiation minimizes the background signal detected by the PMT from the scattered probing radiation. LIF spectroscopy provides high sensitivity due to its background free nature.

2.1.2 Moderate Resolution LIF Experimental Setup

Figure 2.1 shows the schematic diagram for the LIF setup used for the alkoxy radicals experiment. This setup is similar to the one described previously.^{15, 28, 84, 90-92} The alkyl nitrite was stored in a stainless-steel reservoir and expanded into a vacuum chamber through a 0.5 mm pinhole nozzle with 200 psi of backing pressure of helium gas to create a supersonic jet showing in figure 2.2. A 355 nm photolysis beam generated by the third harmonic of an Nd:YAG laser (Continuum, Powerlite Precision II 8000) was focused at the throat of the expansion to photolyze the O-NO bond of the nitrite precursor near the orifice of the pulsed solenoid nozzle (General Valve, series 9). The free radicals produced were excited to the $\tilde{B}$ electronic state by a frequency-doubled pulsed dye laser (Sirah, Cobra-Stretch) pumped by the second harmonic (532 nm) of an Nd:YAG laser (Spectra-Physics, GCR-4) at about a 10 mm downstream distance. The UV probe laser beam was generated by an Nd:YAG (532 nm) pumped dye laser with pyridine 1, pyridine 2, Styryl 8, and DCM (Exciton) laser dyes. The dye laser beam was frequency-doubled (by a KDP crystal)) to provide a tunable output to scan in the 27000-32200 cm^{-1} frequency range. For the LIF measurement, the fluorescence was focused onto a photomultiplier tube (PMT,

Hamamatsu, H10721-01). The PMT output was integrated by a boxcar averager (Stanford Research System, SR250) and sent to a PC via an analog-to-digital converter card (AdLink, PCI-9812). All the spectra were calibrated using a wavemeter (HighFinesse, WS-7). A relative frequency error of $< 1.00 \text{ cm}^{-1}$ is expected in the low-resolution survey scans, mainly due to uncertainty in the peak position of different vibrational bands.

2.1.3 Moderate Resolution DF Experimental Setup

In figure 2.1 shows the schematic diagram for the DF setup used for the isobutoxy, 2-methyl-1-butoxy, isopentoxy, and methyl substituted cyclohexoxy radicals experiment. The experimental setup used to obtain DF spectra has also been discussed in detail elsewhere.^{34, 93-99}. For the DF measurement, the fluorescence was focused on and dispersed by a monochromator (Acton Research, SpectraPro 300i) with an 1800 grooves/mm grating with 300 μm entrance size slit and then imaged onto an intensified charge-coupled device (CCD, Princeton Instruments, PI-MAX 512). The image was collected using the WinSpec software. The spectral resolution of the DF spectra is $\sim 30 \text{ cm}^{-1}$.

2.1.4 Radical Production Chemistry

The alkoxy radicals were produced by the photolysis of corresponding alkyl nitrites (RONO) using the third harmonic of an Nd:YAG laser at 355 nm.

Isobutyl nitrite was purchased from Sigma-Aldrich and used without further purification, while 2- methyl-1-butyl nitrite, isopentyle nitrite, and methyl cyclohexyl nitrites were synthesized by following well-established alkyl nitrite synthesis procedure described by Blatt.¹⁰⁰

Briefly, the alkyl nitrite precursors were synthesized by the addition of sulfuric acid and the appropriate alcohol to an aqueous solution of sodium nitrite. 25.1 ml of concentrated (~97%) sulfuric acid was mixed with 100 ml of water. 0.75 mol of appropriate alcohol (1,2,3,4-methylcyclohexanol, isopentanol, or 2-methyl-1-butanol) was added to the sulfuric acid solution. Protons from the acidic solution can form hydrogen bonds with the hydroxy group of the alcohol and make the hydroxy group a better leaving group (Eqn. 2.3).

The sulfuric acid and alcohol mixture was added dropwise to 100 ml of 0.7 M sodium nitrite solution kept at 0°C over a period of about 120 minutes. The nitrite group then removes the hydroxy group from the alcohol in a substitution reaction to give the alkyl nitrite precursor (Eqn. 2.4).

Alkyl nitrite was then separated from the aqueous layer using a separatory funnel. All the chemicals for the synthesis were purchased from Sigma-Aldrich. There are minor impurities, mainly solvent, but they were not expected to dissociate with the 355nm photolysis laser. All observed LIF signals are dependent on the photolysis laser.

2.2 Cavity Ring-Down Spectroscopy (CRDS)

Alkyl peroxy radicals possess a strong $\tilde{B}-\tilde{X}$ electronic transition in the UV, which has been used to follow them in various kinetics experiments. However, the $\tilde{B}$ -state is dissociative, leading to a broad and structure-less spectrum, as is characteristic of all peroxy radicals, making the UV transition a poor diagnostic to selectively identify different peroxies or to use to characterize the geometric and electronic structure of the molecule.^{82, 101} Unlike the $\tilde{B}$ -state, the $\tilde{A}$ -state is bound. Thus, the $\tilde{A}-\tilde{X}$ transition yields spectra with a well-defined structure allowing one to distinguish between different peroxy radicals as well as different isomers and conformers of a given peroxy radical. Miller and coworkers have identified several alkyl peroxy radicals via their $\tilde{A}-\tilde{X}$ electronic transitions in the near-infrared (NIR) using CRDS.¹⁰² Moderate to high-resolution NIR-CRDS experiments have been performed for several peroxy radicals to give accurate transition energies, vibrational frequencies, and rotational constants.¹⁰²⁻¹⁰⁴ Thus, the CRDS technique was used to obtain the spectrum for the $\tilde{A}-\tilde{X}$ transition of methyl allyl peroxy results of which are presented in Chapter VII of this dissertation.

2.2.1 Introduction

Cavity ring-down spectroscopy (CRDS) is a simple, highly sensitive direct absorption technique based on the rate of absorption of light circulating in an optical cavity. CRDS can be used to study atoms and molecules in the gas and condensed phase and is especially powerful for measuring strong absorptions of species present in trace amounts or weak absorptions of abundant species. The transmitted intensity follows the Beer-Lambert Law

$$I = I_0 \cdot \exp(-\sigma NL) \quad (2.5)$$

where I_0 and I are the incident and transmitted light measured before and after an absorbing species, σ is the absorption cross section of the molecule at a given wavelength, N is the number density of the absorber per unit volume, and L is the path length of light through the absorber. The sensitivity of an experiment depends on the I_0 and I that means how well I and I_0 can be differentiated from each other. In a traditional single pass absorption experiment, I and I_0 are monitored as a function of wavelength. If one is attempting to detect a species that absorbs very weakly and is present in small concentrations, then traditional absorption experiments will not be successful because the difference between I and I_0 is undetectable. Hence, most absorption methods lack the sensitivity needed to investigate weak absorption cross-sections and for low concentrations of the absorbing molecule. Cavity ringdown spectroscopy (CRDS) is a modification of a traditional absorption experiment that utilizes a multipass absorption technique to increase the path length along a physically small dimension effectively.

In CRDS, light is coupled into a high finesse optical cavity made up of two highly reflective mirrors, as shown in Figure 2.3. The fraction of light that is trapped within the

cavity is reflected back and forth between the two mirrors. At each reflection, a small portion of light leaks out of the cavity and is detected. A very small portion of the trapped photons leaks through each of the mirrors on each round trip. The light leaking out of the cavity decreases exponentially with consecutive round trips, and the intensity of the radiation leaked out is measured as a function of time and recorded. The decay curve of the intensity as a function of time is fit to an exponential function, yielding the ring-down time. Beer-Lambert law can be adapted to calculate the fractional loss of the intensity of light in a cavity.

$$I_t = I_0 \cdot \exp \left[- \left(\frac{\text{loss}}{\text{reflection}} \right) \left(\frac{\text{number of reflections}}{\text{round trip}} \right) (\text{number of round trips}) \right] \quad (2.6)$$

The number of reflections per round trip is 2, because of two mirrors in a cavity. The number of round trips (n) in time t would then be given by

$$n = \frac{tc}{2L} \quad (2.7)$$

Where L is the length of the ring down cavity, and c is the speed of light. If R is taken as the reflectivity of the mirrors, then the loss per reflection would be (1-R). Eq. (2.7) can then be modified as

$$I_t = I_0 \cdot \exp \left[- (1-R) \left(\frac{tc}{L} \right) \right] \quad (2.8)$$

The intensity of light (I_t) then decays with a time constant, viz, the empty-cavity ring-down time, τ_0 , which is defined as the time for the intensity to decay to the 1/e of the initial intensity (I_0). In an empty cavity, τ_0 is given by

$$\tau_0 = \frac{L/c}{(1-R)} \quad (2.9)$$

When an absorbing sample is introduced inside the cavity, the loss of intensity of light due to absorption is given by

$$\text{absorption loss} = (\text{loss per round trip})(\text{number of round trip}) = (2\sigma Nl) \frac{tc}{2L} \quad (2.10)$$

Where l is the length of the absorbing sample inside the cavity which could be smaller or equal to the length of the cavity L . The total loss in the intensity of light is then given by

$$\text{total loss} = (1-R) \left(\frac{tc}{L} \right) + (\sigma Nl) \left(\frac{tc}{L} \right) = [(1-R) + (\sigma Nl)] \frac{tc}{L} \quad (2.11)$$

Beer-Lambert law for a ring-down cavity with an absorber is therefore:

$$I_t = I_0 \cdot \exp \left\{ - \left[(1-R) + \sigma Nl \right] \left(\frac{tc}{L} \right) \right\} \quad (2.12)$$

The ring-down time of the cavity with the absorbing sample, τ_{abs} , is given by

$$\tau_{\text{abs}} = \frac{L/c}{(1-R) + \sigma Nl} \quad (2.13)$$

Eqn. (2.9) and (2.13) can be then be combined to give

$$\sigma Nl = \frac{L}{c} \left(\frac{1}{\tau_{\text{abs}}} - \frac{1}{\tau_0} \right) \quad (2.14)$$

There are two main benefits of CRDS when compared with typical absorption spectroscopy experiments. The first is the greatly increased effective path length and hence the extremely high sensitivity. For a typical flow-cell CRDS experimental setup, $L=l=0.5$ m, $R=99.995\%$, the empty-cavity ring-down time is 33 μs , and the effective path length is

10 km. Thanks to the long path length, a minimum detectable absorption coefficient of ~0.3 ppm per pass can be achieved.

The second significant advantage of CRDS is the insensitivity to fluctuations in incident radiation intensity. Unlike in traditional multipass absorption spectroscopy, in which intensity of the transmission is used to determine the absorbance, in CRDS, it is determined from change of the decay constant when the absorbing sample is introduced into the cavity.

2.2.2 Room Temperature Experimental Setup

The apparatus for the room temperature experiment is represented in Figure 2.4. The experimental setup used to obtain CRD spectra has also been discussed in detail elsewhere.¹⁰⁵⁻¹⁰⁸ The required NIR radiation, around 1.3 μ m, was generated by a Raman shifting of the output of a dye laser in molecular hydrogen. The second harmonic of Nd:YAG (PRO- 270, Spectra-Physics) is pumping a Sirah dye laser system with a 20 Hz repetition rate. Operated with DCM laser dye (Exciton), the system produced 90-130 mJ/pulse of tunable radiation in the region of 605-640 nm with a linewidth of 0.6 cm^{-1} . Initial frequency calibration was performed with Ocean Optics Wave meter and was typically within a 0.25 cm^{-1} from the dye laser dial reading. Dye laser resolution is limited by the resolution of the dye laser grating. The output of the dye laser was focused by a lens ($f=50$ cm) into a 93 cm long single Raman cell filled with 200-220 psi of H_2 . The output radiation from the Raman cell was spectrally filtered using several 1.0 μ m cut-off longwave filters (Corion LL-1000-F) to eliminate anti-stokes and 1st stokes radiation. The laser beam

is collimated by a telescope consisting of two confocal lenses ($f=7.5$ and 2.5 cm) and before being injected into the ring-down cavity. A $100\text{ }\mu\text{m}$ pinhole is placed at the focal point of the telescope for mode selection. The resulting $1\text{--}2\text{ mJ}$ of the second stokes radiation in the $1.25\text{--}1.35\mu\text{m}$ region was delivered to the ringdown cell through two 50 cm focal length lenses. The ringdown cavity was fabricated of stainless steel and consisted of a 20 cm long central part with two rectangular UV grade quartz photolysis windows and two 15 cm long arms. The cavity ringdown mirrors (purchased from Los Gatos Research Inc.) were positioned at the ends of the arms on adjustable mounts.

An ArF and KrF excimer laser (Lambda-Physik, LPX 120i) were used to provide the 193 nm and 248 nm photons for photolysis. A set of diverging and converging cylindrical lenses was used to reshape the photolysis laser beam cross section to a $12\times 0.5\text{ cm}^2$ rectangle. The fluence of the photolysis beam was measured to be $\sim 50\text{ mJ/cm}^2$. A set of diverging and converging cylindrical lenses was used to reshape the photolysis laser beam cross section to a $12\times 0.5\text{ cm}^2$ rectangle. The fluence of the photolysis beam was measured to be $\sim 50\text{ mJ/cm}^2$. CRD mirrors (Los Gatos Research, $R>99.99\%$) were mounted on both ends of the reaction cell to form a ring-down cavity with a length of $L\sim 55\text{ cm}$. The photolysis laser was sent through the photolysis quartz windows into the central part of the flow cell, thereby determining the volume wherein radicals are created. Under this condition, all infrared photons will interact with produced radicals, and radicals will be distributed uniformly within the probe beam.

The outlet of the flow cell was connected through the needle valve to the vacuum pump. The following procedure was used to determine the pumping speed. Pure nitrogen and oxygen were introduced into the cell through a calibrated mass flow controller (MKS),

and the pressure in the cell was measured against several readings of the flow controller. The voltage from each mass-flow controller was sent to a digital display box. The slope of the obtained pressure vs. gas flow dependence will represent pumping speed. N₂ gas flow carried vapor of methyl-substituted allyl chloride precursors into the reaction cell. Saturation vapor pressure of the precursors was controlled and stabilized by immersing precursor reservoirs in a 1:1 water-ethylene glycol bath (about -10°C). Gas flow rates were as follows: precursor in N₂: 100-200 sccm; O₂: 500-750 sccm. The partial pressure of the N₂ gas flow for purging the CRD mirrors and the UV side windows for the photolysis beam was controlled by a needle valve to ~50 Torr, while the total pressure in the reaction cell was ~150 Torr. The frequency of the dye laser was measured by a wavelength meter (HighFinesse, WS-7, absolute accuracy=60 MHz). The linewidth of the near-IR radiation is estimated to be about 1 GHz.^{109, 110} A Thorlabs InGaAs (CS10) photodiode was used to detect the outcoming radiation in the 1.2-1.7 μm region.

Transmission of the near-IR radiation through the ring-down cavity was focused on and detected with an amplified InGaAs photodiode (Thorlabs, PDA10CS) and recorded with an oscilloscope (Tektronix, DPO3014). The empty-cavity ring-down time was ~150 μs. Averaged ring-down decay curves were sent to a PC and fit by a home-built LabVIEW program. Ring-down decay curves were collected at each wavelength with the excimer photolysis laser on and off. Absorption (in ppm/pass) recorded with the photolysis laser off, i.e., absorption due to precursors was subtracted from that with the photolysis laser on to obtain net absorption due to products. The time delay between the photolysis and the CRD laser pulses can be varied for kinetic measurements. Lifetimes of MAOO· peroxy radicals were measured to be ~1 ms.

2.2.3 Peroxy Radical Production

Methyl allyl peroxy radicals were produced in a room-temperature stainless steel gas-flow reaction cell by 193 nm or 248 nm photolysis of corresponding methyl-substituted allyl chlorides in the presence of excessive O₂. Three commercially available precursors were used: 3-chloro-2-methyl-1-propene (97%, TCI), 3-chloro-1-butene (97%, Sigma-Aldrich), and 75% 1-chloro-2-butene and 25% 3-chloro-1-butene mixture (TCI). Production of methylallyl (MA) radicals by photolysis (Reaction 1) is followed by oxygen addition (Reaction 2) to form the peroxy radicals ROO[•], where R[•] is the MA radical:

The MAOO[•] radical has three isomers (1-, 2-, and 3-MAOO[•]'s). 193 nm photolysis of 3-chloro-2-methyl-1-propene produces the 2-MA radical (Figure 2.5a). It is a resonance hybrid with two contributing structures: CH₂=C(CH₃)CH₂[•] and [•]CH₂C(CH₃)=CH₂. Oxygen addition to either structure forms the 2-MAOO[•] radical.

When 1-chloro-2-butene or 3-chloro-1-butene is used as a precursor, the direct photolysis products are 1-MA radicals with the unpaired electron at the primary (CH₃CH=CHCH₂[•]) and secondary (CH₃CH[•]CH=CH₂) positions, respectively (Figures 2.5b and 2.5c). These are two contributing structures of a resonance-stabilized free radical. The nascent radicals produced by photolysis interconvert *via* allylic rearrangement:

Oxygen additions to both nascent MA radicals produced by photolysis and secondary free radicals *via* allylic rearrangement are possible (Figures 2.5b and 2.5c). Terminal addition produces 1-MAOO $\cdot$:

while non-terminal addition produces 3-MAOO $\cdot$:

The population ratio of 1- and 3- MAOO $\cdot$ radicals produced is therefore determined by the reaction rate constants ($k_{\pm\text{r}}$, $k_{1-\text{MAOO}}$, $k_{3-\text{MAOO}}$) of Reactions 2.17-2.19. Note that we also used 248 nm (KrF excimer) photolysis laser, but no CRD signal of MAOO $\cdot$ was observed. All peaks observed in the CRD spectra that are assigned to MAOO $\cdot$ radicals depend on the presence of the stable precursors and oxygen, 193 nm photolysis laser pulses, and delay time between the photolysis and CRD laser pulses shorter than ~ 3 ms.

PMT=photomultiplier tube;
 OGC=optogalvanic cell
 iCCD=intensified charge coupled device

Figure 2.1. Moderate-resolution LIF/DF apparatus.

Figure 2.2. Supersonic cooling

Figure 2.3. Principle of Cavity ring-down spectroscopy.

Figure 2.4. A schematic of Room Temperature CRDS apparatus.

Figure 2.5. Schematics of production of (a) 2-MAOO $\cdot$ radical using 3-chloro-2-methyl-1-propene as the precursor, and 1- and 3-MAOO $\cdot$ radicals using either (b) 1-chloro-2-butene or (c) 3-chloro-1-butene as the precursor. Bidirectional arrows denote allylic rearrangement.

CHAPTER III

THEORY OF SPECTRAL SIMULATION

3.1 Introduction

Electronic spectra of polyatomic molecules are more complicated than those of the diatomic molecules for various reasons. First, the number of vibrational modes in a polyatomic molecule is $3N-6$ ($3N-5$ in a linear molecule), where N is the number of atoms in the molecule. Therefore, the larger the number of atoms in the molecule, the larger the number of vibrational modes, and hence the more congested the electronic spectrum is due to more vibronic (vibrational-electronic) transitions. The spectral congestion is further exacerbated by more complicated molecular geometry and often lower molecular symmetry, which introduces more allowed vibronic transitions. Moreover, polyatomic molecules usually have three rotational constants, whereas diatomic molecules have only one rotational constant. (For diatomic molecules, the two rotational constants for rotations around the two principal axes perpendicular to the internuclear axis are identical). Usually, polyatomic molecules have larger moment of inertia and, hence, smaller rotational constants than diatomic molecules. As a result, the rotational levels of medium to large-sized polyatomic molecules are so close to each other that the rotational and fine structure of their vibronic transitions cannot be resolved

using nanosecond pulsed lasers (typical linewidth $\sim 0.1 \text{ cm}^{-1}$). Finally, the spectra of polyatomic molecules can be complicated by the existence of multiple conformations, as we shall see in this Dissertation. It is, therefore important to review the basic theory and methodology for prediction and simulation of vibronic spectra of polyatomic molecules. In such spectral prediction and simulation, both the transition frequencies (i.e., transition energies) and transition intensities need to be calculated, which we will discuss in the rest of this chapter.

3.2 Energy Level Structure of Polyatomic Molecules

3.2.1 Born–Oppenheimer (BO) Approximation

The Born–Oppenheimer Principle (or Born–Oppenheimer Approximation) states that the electrons in a molecule move so much faster than the nuclei that the two kinds of motion are independent: the electrons see the nuclei as being stationary, and so each electron doesn't have to adjust its motion to maintain a minimized electron–nucleus interaction energy. Thus, we can calculate the purely electronic energy of a molecule at different molecular geometries, then the internuclear repulsion energy, and add the vibrational energies of nuclei to get the total molecular energy. If we assume the nuclei and electrons in a molecule to be point masses and neglect spin-orbit and other relativistic corrections, then the molecular Hamiltonian can be written compactly by this equation

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{en} + \hat{V}_{ee} \quad (3.1)$$

The first two terms in Eq. (3.1) are the kinetic energy operators of the nuclei (T_n) and electrons (T_e), respectively, the third term is the potential energy of repulsion between the

nuclei (V_{nn}), the fourth term is the potential energy of attraction between the electrons and the nuclei (V_{en}), and the fifth term is the potential energy of repulsion between the electrons (V_{ee}).

The nuclear kinetic energy (T_n) can be separated from the total molecular Hamiltonian, the rest terms of the molecular Hamiltonian (Eq. 3.1) can be written as $H_{el}+V_{nn}$, where $H_{el}=T_e+V_{en}+V_{ee}$ is the pure electronic Hamiltonian. The Schrodinger equation with $H_{el}+V_{nn}$ is

$$(H_{el}+V_{nn})\Psi_{el}=U\Psi_{el} \quad (3.2)$$

In Eq. (3.2), U is the electronic energy, including internuclear repulsion. Under the Born-Oppenheimer Approximation, Ψ_{el} is a function of *only* electronic coordinates. Therefore, the contribution of V_{nn} to molecular energy is a constant shift of all energy levels at each molecular geometry. One can, therefore, further separate V_{nn} from the total molecular Hamiltonian. Eq. (3.2) reduces to:

$$H_{el}\Psi_{el}=E_{el}\Psi_{el} \quad (3.3)$$

where E_{el} is the pure electronic energy of the molecule. E_{el} and Ψ_{el} can be solved *ab initio*, followed by calculation of the vibrational energy level structure of each electronic state at fixed nuclear coordinates.

3.2.2 *ab initio* Computations

Numerous calculations have been done to predict and simulate LIF and DF spectra of alkoxy radicals and CRDS spectra of peroxy radicals. These computational data include i) the $\tilde{B}-\tilde{X}$ adiabatic excitation energies of alkoxy radicals and the $\tilde{A}-\tilde{X}$ adiabatic excitation

energies of peroxy radicals, ii) vibrational modes and frequencies in all aforementioned electronic states, especially the C–O stretch of alkoxy radicals and the O–O stretch of the peroxy radicals; and iii) relative energies of different isomers and conformers of each investigated molecule in their ground states. Density functional theory (DFT) method using the B3LYP,¹¹¹ or CAM-B3LYP¹¹² functionals has been used for the ground electronic ($\tilde{X}$) state calculations, while the $\tilde{B}$ state of alkoxy radicals and the $\tilde{A}$ state of peroxy radicals were calculated using the configuration interaction single (CIS)¹¹³ and time depended (TD-)DFT methods. For molecules with the C_s symmetry, the first excited state (the ground state of its own symmetry) can be calculated using the DFT method with the HOMO and LUMO orbitals of the unpaired electron swapped. (See Section 4.2) For low-lying electronic states, the adiabatic excitation energy calculated using the DFT method is significantly more accurate than those calculated using the CIS or TD-DFT method.

All calculations have been performed by the Gaussian09 program,¹¹⁴ using standard basis sets, including 6-31+G (d), 6-311+G(d,p).

3.2.3 Molecular Vibrations

In the research reported in the present dissertation, harmonic frequencies of vibrational modes of involved electronic states are calculated *ab initio*. Energies of vibrational levels of each electronic state with respect to the minimum of the potential energy surface (PES) is, therefore:

$$E_v = \sum_{i=1}^{3N-5 \text{ or } 3N-6} \left(v_i + \frac{1}{2}\right) h\nu_i \quad (3.4)$$

where v_i and v_i are the vibrational quantum number and harmonic vibrational energy of the i^{th} vibrational mode, respectively. Usually, vibrational energies are given in the form of the wavenumber and in the unit of cm^{-1} . In this case, $h\nu$ is replaced by the harmonic frequency ω_e , and the wavenumber of a vibrational level with respect to the minimum of the electronic state is:

$$G_v = \sum_{i=1}^{3N-5 \text{ or } 3N-6} (v_i + \frac{1}{2}) \omega_{e,i} \quad (3.5)$$

In real molecules, the vibrational energy level structure is affected by the vibrational anharmonicity. With anharmonicity, high-order terms are included in Eq. (3.5):

$$G_v = \sum_{i=1}^{3N-5 \text{ or } 3N-6} \left[(v_i + \frac{1}{2}) \omega_{e,i} - (v_i + \frac{1}{2})^2 \omega_{e,i} x_{e,i} + (v_i + \frac{1}{2})^3 \omega_{e,i} y_{e,i} + \dots \right] \quad (3.6)$$

Usually, we truncate the equation above after the first two terms in the squared brackets, i.e., only the harmonic term and the first-order anharmonic correction ($x_e \omega_e$) are taken into account. The energy separation between the v and the $v+1$ levels is, therefore:

$$\Delta G_{v+1/2} = G_{v+1} - G_v = \omega_e - 2\omega_e x_e \quad (3.7)$$

The discrete values $\Delta G_{v+1/2}$ as a function of v_i define a straight line (eq 3.7) with a y-axis intercept of ω_e and a slope of $-2\omega_e x_e$. This plot is called the Birge-Sponer plot. From fitting the Birge-Sponer plot of experimental data, the harmonic frequency ω_e and the anharmonicity parameter x_e can be determined.^{115, 116}

To calculate the vibrational frequencies of a molecule, first, we need to find its equilibrium geometry (within the Born-Oppenheimer approximation). Second, the potential energy

surface (PES) is expanded in the Taylor series. The zeroth-order is defined as zero. The first order is 0 because of the minimum energy condition. The calculation of second derivatives of the potential energy surface leads to the molecular Hessian, which enables the prediction of vibrational frequencies.¹¹⁷

Note that every vibrational mode contributes to the zero-point energy (ZPE):

$$E_0 = \sum_{i=1}^{3N-5 \text{ or } 3N-6} \frac{1}{2} h\nu_i \quad (3.8)$$

The ZPEs offset the $\nu=0$ levels of electronic states from the minima of their PESs and have to be taken into account in calculating the adiabatic electronic transition frequencies ($\nu'=0 \leftarrow \nu''=0$).

3.3 Transition Intensity

The transition intensity between two energy levels is proportional to the line strength (S), as well as the lower- and upper-state populations. For an excitation, i.e., an upward transition:

$$I \propto S(N''-N') \quad (3.9)$$

where N' and N'' are the lower and upper state populations, respectively. For electronic transitions, $N'' \gg N'$. The equation above can be written as:

$$I \propto SN'' \quad (3.10)$$

The transition intensity is also proportional to the intensity of the excitation laser, if the transition is not saturated. In our experiments, we use a constant excitation laser intensity

whenever possible. Otherwise, the experimental spectra are normalized by the laser intensity.

3.3.1 Separation of the electric transition dipole moment and the Franck-Condon Factor

The line strength (S) can be written by the following equation:

$$S \propto (\int \Psi' |\hat{\mu}| \Psi'' d\tau)^2 \quad (3.11)$$

where Ψ'' and Ψ' are overall wave functions of the lower and upper states, respectively. They are products of the electronic, vibrational, and spin wave functions. (Rotational and nuclear spin wavefunctions are neglected in the present research.) $\Psi = \Psi_e \Psi_v \Psi_s$. $\hat{\mu}$ is the molecular dipole moment (operator), consisting of the electronic and the nuclear components, i.e., $\hat{\mu} = \mu_e + \mu_N$. under the Born-Oppenheimer Approximation, we can separate the electronic and the nuclear wavefunctions. The spin wavefunctions are also treated separately. Upon the separation of the electronic, vibrational, and spin wavefunctions, Eq. (3.11) becomes

$$S \propto (\int \Psi'_e \Psi'_v \Psi'_s |(\mu_e + \mu_N)| \Psi''_e \Psi''_v \Psi''_s d\tau)^2 \quad (3.12)$$

$$S \propto (\int \Psi'_v \Psi''_v d\tau \int \Psi'_e |\mu_e| \Psi''_e d\tau \int \Psi'_s \Psi''_s d\tau + \int \Psi'_e \Psi''_e d\tau \int \Psi'_v |\mu_N| \Psi''_v d\tau \int \Psi'_s \Psi''_s d\tau)^2 \quad (3.13)$$

The second term in the parentheses in Eq. 3.13 vanishes under the Born-Oppenheimer Approximation because electronic wavefunctions of different electronic states are eigenfunctions of the pure electronic Hamiltonian H_{el} and, hence, orthogonal to each other. The remaining (first) term

$$S \propto (\int \psi'_v \psi''_v d\tau \int \psi'_e |\boldsymbol{\mu}_e| \psi''_e d\tau \int \psi'_s \psi''_s d\tau)^2 \quad (3.14)$$

is the product of three integrals. The first integral ($\int \psi'_v \psi''_v d\tau$) is the overlap integral between the vibrational wavefunctions of the two states, and its square is called the Franck–Condon factor. The second integral ($\int \psi'_e |\boldsymbol{\mu}_e| \psi''_e d\tau$) is the electric transition dipole moment between the upper and lower electronic states. The third integral ($\int \psi'_s \psi''_s d\tau$) involves the electron spin and leads to the spin selection rule of $\Delta S=0$, where S is the electron spin.

3.3.2 Franck-Condon factor

To calculate the intensities of transitions between different vibrational states of two electronic states, the Franck-Condon (FC) principle may be applied.^{118, 119} When a molecule undergoes an electronic transition, the nuclear configuration of the molecule experiences no significant change because that nuclei are much more massive than electrons, and the electronic transition takes place faster than the nuclei can respond. The Franck-Condon principle is, therefore, also called the vertical transition principle.

Due to the Franck-Condon principle, vibrational bands in an electronic transition vary in intensity, in proportional to the square of the first integral $(\int \psi'_v \psi''_v d\tau)^2$ in equation (3.14), which is called the Franck-Condon factor (FCF) for the transition. Figure 3.1¹²⁰ shows the vibrational wave functions for some vibrational levels of two electronic states of a diatomic molecule that have different values of R_e , the internuclear distance at the equilibrium. Consider a transition from the $v''=0$ vibrational level of the ground electronic state to a vibrational level of the excited electronic state. From the figure, we see that Ψ''_v for $v''=0$ and Ψ'_v for $v'=2$ are both large at the same value of R ; hence these two functions have optimal overlap, and the $v=2 \leftarrow 0$ vibrational band of the electronic transition should be the most intense band (in the absorption or excitation spectrum). Similarly, emission from the $v' = 2$ level of the excited electronic state gives an intense band for the transition to the $v''=0$ level.

3.2.3 Computation of Franck-Condon factors and the Duschinsky Mixing

In the research reported in the present dissertation, FCFs were calculated using the ezSpectrum program.¹²¹ Due to the large difference in $\tilde{X}$ -, $\tilde{A}$ - and $\tilde{B}$ -state geometries, Duschinsky rotations were taken into account in the calculation of FCFs to better reproduce the experimental spectra, as explained below.

The normal coordinates of different electronic states of a molecule are usually different due to different molecular geometries and force constants. Thus, electronic transitions can cause mixing of normal modes, i.e., a specific normal mode of the excited electronic state is a linear combination of two or more normal modes of the ground

electronic state and vice versa. In the multi-dimensional space comprising of the normal modes, this mixing is presented as a rotation of the normal coordinates. This phenomenon was first considered by Duschinsky¹²² when extending the FC principle from diatomic to polyatomic molecules. Duschinsky first proposed that the two sets of normal coordinates are related to each other by a unitary transformation and a displacement vector. (See figure 3.2). The vector gives the displacement between the equilibrium structures of the two states, and the unitary transformation matrix can be viewed as an overlap matrix between the normal modes of the two electronic states.¹²³ The closer the squares of the diagonal elements are to unity, the more the normal modes are like each other in form and energy. Large off-diagonal elements indicate a change in the energy ordering or mixing between different normal modes. This mixing is the mathematical expression of a Duschinsky rotation.

3.3.3 Boltzmann Distribution

The intensities of lines in a vibronic spectrum also depend on the population of the lower state. For room-temperature experiments, the Boltzmann distribution is used to predict the relative populations of different molecules, different isomers, and conformers of a certain molecule, and different vibrational levels of a certain molecular species. The expression for such calculation is:

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-E_i/kT} \quad (3.14)$$

where n_0 and n_i are populations of the ground and the i^{th} excited state, respectively. g_i and g_0 are degrees of degeneracy of the two states. E_i is the relative energy of the i^{th} excited

state (with respect to the ground state). When multiple molecular species (including conformers and isomers) co-exist, n_0 refers to the ground state of the lowest-energy species, while E_i is relative to this lowest state.

We can write the Boltzmann distribution as

$$p_i = \frac{g_i e^{-E_i/kT}}{q} \quad (3.15)$$

where p_i is the molar fraction of a molecule in state i , $p_i = n_i/n_{\text{total}}$, where n_{total} is the total population of all molecular species (in all states). q is the molecular partition function:

$$q = \sum_i g_i e^{-\frac{E_i}{kT}} \quad (3.16)$$

It is important to note that the application of the Boltzmann distribution assumes that molecular species are at thermal equilibrium. In our experiments, free radicals are produced from stable molecules. In the room-temperature CRD experiment (see Section 2.2.2), thermal equilibrium is a fairly good approximation because of the relatively high temperature and high pressure. Nascent free radicals reach the thermal equilibrium via collision with buffer gas molecules (N_2). In the jet-cooled LIF/DF experiments, free radicals may be “trapped” in local maxima of the PES due to insufficient collisions with the carrier gas molecules (He or Ar) before entering the collision-free zone, where they are interrogated by the laser beam. Boltzmann distribution is, therefore, not a good approximation for predicting relative populations in jet-cooled experiments.

Figure 3.1. Franck–Condon principle energy diagram taken from ref. [119]. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v = 2$.

Figure 3.2. Duschinsky mixing between to normal modes can be presented as a rotation of the vibrational normal coordinates. $Q = \frac{1}{2\pi} \sqrt{\frac{2h}{v\mu}} (v + \frac{1}{2})$, where Q'' and Q' are the normal coordinates of the ground state and the excited state, respectively. h is the Planck's constant, μ is the reduced mass, and v is the vibrational quantum number. Adapted from ref. [121].

CHAPTER IV

DISPERSED FLUORESCENCE SPECTROSCOPY OF JET-COOLED ISOBUTOXY AND 2-METHYL-1-BUTOXY RADICALS

4.1 Introduction

Alkoxy radicals are important reaction intermediates in the combustion of fossil fuels³ and the atmosphere, especially in the troposphere.^{1,2} Extensive investigations have been carried out to explore the chemical kinetics involving alkoxy radicals.^{6, 124-127} In the atmosphere, alkoxy radicals are formed in the degradation of volatile organic compounds (VOCs) typically initiated by reaction with an OH radical and in the presence of NO_x. They can undergo several reaction paths: reaction with O₂, unimolecular dissociation (decomposition by β C-C bond fission), and isomerization, for example, via a 1,5 H-shift. Alkoxy radicals, therefore, constitute a critical branching point in the oxidation of VOCs.

Most alkoxy radicals have multiple structural and conformational isomers. It is well known that rate constants of alkoxy reactions can be highly sensitive to their conformations in the ground and excited states. For instance, the energy barrier for the isomerization of ground-state 1-butoxy (a 1,5 H-shift) is 3.6 kcal/mol lower than decomposition, whereas the barrier of isobutoxy isomerization (a 1,4 H-shift) is 10.6 kcal/mol higher than that of decomposition. This is due to the fact that the isomerization of isobutoxy occurs via a six-

membered transition state, while the transition state of 1- butoxy isomerization contains a five-membered ring that has higher strain energy and is less stable. Eventual stable products of particular hydrocarbon oxidation are determined by the competition between various potential reaction pathways of alkoxy radicals. Conformation-specific studies of alkoxy radicals, especially that of the correlation between their structures and their reactivities, are, therefore, of significant importance to atmospheric chemistry.

Previously, Jin *et al.*³⁴ reported dispersed fluorescence (DF) spectra of 1- and 2-butoxies, in which vibrational structure of both the ground electronic ($\tilde{X}$) state and the first excited electronic ($\tilde{A}$) state revealed itself in the DF spectra, along with the energy separation between the zero-point levels of these two states $\Delta E^{\tilde{A}-\tilde{X}}$. Significant differences are observable when the DF spectra of these two isomers are compared: in the DF spectra of 2-butoxy, there are fewer individual lines in the low-frequency region and lines become broader and more congested in the high-frequency region when compared to 1-butoxy. Such differences are attributed to the smaller $\tilde{A}-\tilde{X}$ separation for 2-butoxy than 1-butoxy, which was also used to explain the more irregular vibrational progressions in 2-butoxy.

Recently, our group observed the DF spectra of t-butoxy. Because of its high symmetry (C_{3v}), the ground electronic state of t-butoxy is orbitally doubly degenerate, albeit split by the spin-orbit interaction to two components ($\tilde{X}^2E_{3/2}$ and $\tilde{X}^2E_{1/2}$) with their zero-point levels separated by 36 cm^{-1} . The ground state of t-butoxy is also subject to the Jahn-Teller (JT) effect that couples the two degenerate vibronic state $|ev_x\rangle$ and $|ev_y\rangle$. Despite such complications, it was possible to assign almost all observed DF lines aided by vibrational frequencies and Franck-Condon factors (FCFs) calculated by the complete active space self-consistent field (CASSCF) method.

It is therefore of interest to obtain the DF spectra of isobutoxy (2-methyl-1-propoxy), the first target molecule of the present work, and make comparison with the other three isomers. Experimentally observed DF spectra elucidate the energy level structure of the $\tilde{X}$ and $\tilde{A}$ states and can be used to test the conformational assignment of the laser-induced fluorescence (LIF) spectrum previously reported by Liang *et al.*,²⁹ in which five vibronic bands of the $\tilde{B} \leftarrow \tilde{X}$ transition were observed. Because no rotational structure was resolved in the LIF spectrum, the conformational and vibrational assignments completely relied on ab initio calculations. Comparing between DF spectra obtained by pumping different vibronic bands in the LIF spectrum, one can differentiate LIF peaks of different conformers. Furthermore, comparison between the experimentally obtained transition frequencies in DF spectra and the calculated ground-state vibrational frequencies of different conformers allows a more reliable conformational assignment than that based on the comparison between LIF spectra and the calculated excited-state vibrational frequencies because calculations of ground-state vibrational frequencies are in general more accurate than the excited state. The DF spectra may also reveal the $\tilde{A}-\tilde{X}$ separation directly.

Chemical reactivities and branching ratios can also be affected by methyl substitution. In addition to isobutoxy, Ref. [29] reported the LIF spectrum of 2-methyl-1-butoxy. Because of the longer carbon-chain than isobutoxy, a six-membered transition state for 1,5 H-shift is possible for 2-methyl-1-butoxy. Different branching ratios between the different reaction pathways are therefore expected for 2-methyl-1-butoxy and isobutoxy. It would also be interesting to compare the energy level structure of 2-methyl-1-butoxy to that of 1-butoxy and 2-butoxy, which may provide more information that will help explain

the difference between their DF spectra. DF spectra of 2-methyl-1-butoxy were therefore obtained in the present work as well.

4.2 Quantum Chemical Calculations

Previously, geometry optimization and frequency calculation of both the $\tilde{X}$ and $\tilde{B}$ states of different conformers of isobutoxy and 2-methyl-1-butoxy radicals were performed using the Density Functional Theory (DFT) and CASSCF methods and the results were used for assignment of LIF spectra.²⁹ We have carried out same quantum chemical calculations in order to predict the Franck-Condon factors (FCFs) and simulate the $\tilde{B}-\tilde{X}$ and $\tilde{B}-\tilde{A}$ DF spectra. It was found that simulation using the DFT results reproduce the experimental spectra significantly better than the CASSCF results. All simulations reported in the present paper, therefore, use the DFT-calculated results at the B3LYP/6-31+G(d) level of theory for the $\tilde{X}$ -state. The $\tilde{B}$ state geometry and vibrations were calculated using the Configuration Interaction Singles (CIS) method with the 6-31+G(d) basis set.

In the DF spectra, the energy separation between the $\tilde{X}$ and $\tilde{A}$ states ($\Delta E^{\tilde{A}-\tilde{X}}$) may be observed directly (section 4.1.3). For molecules with C_s symmetry, this separation can be predicted from quantum chemical calculations by demanding the unpaired electron occupy either of the $2p\pi$ orbitals localized at the oxygen atom: an unpaired electron in the p_x orbital (within the C_s plane) corresponds to an A' state, while the p_y orbital (out of the C_s plane) is half-filled in an A" state. For isobutoxy, only one of its two conformers has C_s symmetry. The calculations predict that its ground electronic ($\tilde{X}$) state has A" symmetry whereas the first excited state ($\tilde{A}$) is of A' symmetry. The energy separation between these two states has been found to be 401 cm^{-1} without zero-point energy (ZPE) corrections. The 2-methyl-1-butoxy radical does not have C_s conformers. Hence no calculation of its $\Delta E^{\tilde{A}-\tilde{X}}$

was attempted.

All DFT and CIS calculations were performed using the Gaussian09 package.¹²⁸ FCFs and transition intensities were predicted using the ezSpectrum software.¹²¹ Due to the significant difference between the $\tilde{X}/\tilde{A}$ and the $\tilde{B}$ state geometries, especially the large increase in the CO bond length upon excitation (e.g., from 1.37 to 1.56 Å for isobutoxy), the Duschinsky rotation was taken into account in simulating the DF spectra.^{122, 123, 129}

4.3 Results

DF spectra were obtained by pumping four vibronic bands of isobutoxy in its LIF spectrum (Bands A-D) and two LIF bands of 2-methyl-1-butoxy radicals (Bands A and B). The LIF bands are labeled following ref. [29] Their transition frequencies are listed in Table 4.1.

4.3.1 Isobutoxy

4.3.1.1 Conformational Assignment

DF spectra of isobutoxy are shown in Figure 4.1. Spectra obtained by pumping Band B, C, and D are similar to one another, all dominated by a vibrational progression of strong sharp peaks separated by $\sim 1000\text{ cm}^{-1}$. DF spectrum pumping Band A is significantly different. Although it also contains a progression, each member of the progression consists of multiple strong peaks. Furthermore, the first strong peak with a nonzero redshift (the second in the vibrational progression, i.e., $\nu = 1$) in the DF spectrum obtained by pumping band B does not match any of the peaks in the second member of the progression that is seen in the DF spectrum obtained by pumping band A (Figure 4.5). Bands B–D and band

A are therefore assigned to different conformers of the isobutoxy radical.

Isobutoxy has two stable conformers, with C_s and C_I symmetry. In Figure 4.2, simulated DF spectra of the $\tilde{B} \rightarrow \tilde{X}$ transitions of the two conformers are compared with the spectra that were obtained experimentally by pumping bands A and B in the LIF spectrum. Although the DF spectrum obtained by pumping band A (at 28091 cm^{-1}) is relatively more complicated, an excellent match has been found between the experimental spectrum and the one simulated using the calculated vibrational frequencies and FCFs of the C_s conformer. The simulated spectrum for the C_I conformer reproduces the strong features in the experimental spectrum obtained by pumping band B (at 28787 cm^{-1}). A better match could be reached if anharmonicity was taken into account (see below). On the basis of the comparison between the experimental and simulated spectra, bands A and B (the first two LIF peaks of isobutoxy) are assigned as the origin bands of the C_s and C_I conformers, respectively.

4.3.1.2 Vibrational Assignment

DF spectra obtained by pumping bands A and B are both dominated by strong vibrational progressions starting from the zero redshifts. For the spectrum obtained by pumping band B (origin band of the C_I conformer), a linear fit of the ground-state vibrational energy level separation $[\Delta G(v)]$ yields a harmonic frequency of $\omega_e = 1060 \pm 5\text{ cm}^{-1}$ and an anharmonic parameter of $\omega_e\chi_e = 5.6 \pm 0.8\text{ cm}^{-1}$ (Table 4.6 and Figure 4.6). In comparison, the calculated harmonic frequency of the CO stretch mode of the C_I conformer is 1073 cm^{-1} . The strong peaks in the spectrum are therefore assigned to the CO stretch progression. This is consistent with the prediction that the DF spectra of alkoxy radicals have strong CO stretch

transitions because of the elongation of the CO bond upon $\tilde{B} \leftarrow \tilde{X}$ excitation, which results in large FCFs for transitions to the CO stretch levels.

Bands C and D are also assigned to the C_I conformer. Although all are dominated by a strong progression, the most noticeable difference between the DF spectrum obtained by pumping band B and those obtained by pumping bands C and D is that the strong progressions in the latter do not start from the zero redshift $\tilde{B} \rightarrow \tilde{X}$ origin band but rather from a low-frequency DF peak, labeled bands “c” and “d” in Figure 4.1. Therefore, if the DF spectra pumping bands C and D are blueshifted by the vibrational frequencies of bands c and d, respectively, the strong progressions in these two spectra will line up with the progression in the DF spectrum pumping band B, as shown in Figure 4.3. It is worth noting that the vibrational interval of band c (129 cm^{-1}) is almost identical to that of band C (130 cm^{-1}), while the vibrational interval of band d (258 cm^{-1}) is close to that of band D (238 cm^{-1}). Bands c and C are therefore assigned to the same vibrational mode ($-\text{CH}_2\text{O}$ wagging; see Figure 4.7a) of the $\tilde{X}$ and the $\tilde{B}$ states, respectively. In the same way, bands d and D are assigned to the in-phase CH_3 torsional mode of the two states (Figure 4.7b). Progressions in the DF spectra pumping bands C and D are combination bands of CO stretch and the pumped vibrational modes. Such a phenomenon was observed in the DF spectra of cyclohexoxy³⁵ as well as 2-, 3-, and 4- methylcyclohexoxy⁹³ (but not 1-methylcyclohexoxy) and is an indication of large Duschinsky rotation upon excitation from the $\tilde{X}$ state to the $\tilde{B}$ state because of the large elongation of the CO bond and Duschinsky mixing between the CO stretch and certain non-CO stretch vibrational modes.^{122, 123}

For the DF spectrum obtained by pumping the C_s conformer origin band (band A), each member of the vibrational progression consists of multiple strong peaks. The second

member of the CO stretch progression ($\nu = 1$) consists of two strong peaks that are reproduced in the simulation as well as several weaker peaks. Inspection of the calculated vibrational modes shows that the two strong peaks (1010 and 1078 cm^{-1} , labeled “y” and “z” in Figure 4.2) can be assigned to vibrational modes with strong CO stretch character but mixed with the umbrella modes (ν_{14} and ν_{13}). The relatively weak peak at 940 cm^{-1} (peak x in Figure 4.2) is attributed to a vibrational mode that mixes the CH_3 scissor and the C–C stretch (ν_{15}), while the weak peak at 824 cm^{-1} (peak “w” in Figure 4.2 and not reproduced in simulation) is attributed to the umbrella mode involving all four carbon atoms (ν_{16}). (See Figure 4.8 for vibrational modes and calculated frequencies.) DF peaks in other members of the progression can be assigned to overtones and combinations of these four vibrational modes. Weak transitions between members of the CO stretch progression are combination bands of CO stretch modes and other low-frequency vibrational modes according to simulation.

Frequencies of strong transitions in the DF spectra of isobutoxy are summarized in Tables 4.2 and 4.3 and compared with the calculated values. Vibrational modes observed in the DF spectra are illustrated in Figures 4.7 and 4.8 for the C_I and C_s conformers, respectively.

4.3.1.3 $\tilde{A}$ – $\tilde{X}$ Separation

When the origin band of the C_s conformer (band A) is pumped, there is a peak at a 426 cm^{-1} redshift in the DF spectrum that is not reproduced in the simulated $\tilde{B} \rightarrow \tilde{X}$ spectrum (Figure 4.2). DFT calculations predict an $\tilde{A}$ – $\tilde{X}$ separation of 401 cm^{-1} for the C_s conformer. The DF peak at 426 cm^{-1} is therefore assigned to the origin band of the $\tilde{B} \rightarrow \tilde{A}$ transition

of the C_s conformer. Similarly, the weak peak at a 373 cm^{-1} redshift in the DF spectrum obtained by pumping band B is assigned to the origin band of the $\tilde{B} \rightarrow \tilde{A}$ transition of the C_I conformer.

4.3.2 2-Methyl-1-butoxy

DF spectra were recorded by pumping bands A (at 28097 cm^{-1}) and B (at 28721 cm^{-1}) in the LIF spectrum of 2-methyl-1-butoxy (Figure 4.4). Both spectra are dominated by two strong progressions. The redshift frequencies, however, are different for the two spectra, which suggests the assignment of bands A and B to two different conformers.

2-Methyl-1-butoxy has nine conformers.²⁹ The conformers are named according to their $\text{OC}_2\text{C}_3\text{C}_4$ and $\text{C}_2\text{C}_3\text{C}_4\text{C}_5$ dihedral angles. DFT calculations predict that the two lowest-energy ones are the G_1T_2 and the T_1T_2 conformers, with the latter being 0.05 kcal/mol higher in energy than the former. The next lowest-energy conformer (T_1G_2') is significantly higher in energy (0.24 kcal/mol higher than G_1T_2). Hence, the $\tilde{B} \rightarrow \tilde{X}$ DF spectra of G_1T_2 and T_1T_2 conformers were simulated and are compared with experimentally obtained spectra in Figure 4.4. Experimentally, broadening and congestion of lines are more significant in the DF spectrum obtained by pumping band A than that for band B. In simulations, the spectrum of T_1T_2 has strong transitions to two vibrational modes (ν_{30} and ν_{28}), both of which have CO stretch character but are mixed with the C–C stretch modes. These two transitions are consistent with the two partially resolved peaks at 1017 and 1078 cm^{-1} observed in the DF spectrum obtained by pumping band A (labeled y and z in Figure 4.4). On the contrary, in the simulated DF spectrum of G_1T_2 , only a single strong CO stretch transition (ν_{28}) is predicted for each member of the progression,

corresponding to the strong peak at 1053 cm^{-1} in the DF spectrum obtained by pumping band B. Band A is therefore assigned to the T_1T_2 conformer and band B to the G_1T_2 conformer. In both cases, DFT calculations predict CO stretch frequencies with high accuracy. For the G_1T_2 conformer, a linear fit of the first four ground-state vibrational energy levels yields a harmonic frequency of $\omega_e = 1075 \pm 8\text{ cm}^{-1}$ and an anharmonic parameter of $\omega_e\chi_e = 9.2 \pm 1.5\text{ cm}^{-1}$ (Table 4.7 and Figure 4.9), compared to the calculated value of 1053 cm^{-1} .

Members of the second (higher-frequency) progressions in DF spectra of both conformers of 2-methyl-1-butoxy have a constant separation with respect to those of the CO stretch progression. They are assigned to combination bands of the CO stretch and other non-CO stretch modes based on FCF calculations, although their intensities are underestimated by the calculations. According to the FCF calculations, the strongest transitions in the second progression in the DF spectrum of the T_1T_2 conformer are combination bands of the CO stretch and the $C_2C_3C_4$ bending mode (ν_{43}), while those in the DF spectrum of the G_1T_2 conformer are combination bands of the CO stretch and methyl torsional modes (ν_{43} and ν_{42}). (See Figures 4.10 and 4.11 for vibrational modes and calculated frequencies.)

Frequencies of strong transitions in the DF spectra of 2-methyl-1-butoxy are summarized in Tables 4.4 and 4.5 and compared with the calculated values. Vibrational modes observed in the DF spectra are illustrated in Figures 4.10 and 4.11 for the T_1T_2 and G_1T_2 conformers, respectively.

4.4 Discussion

In the present work, for both isobutoxy and 2-methyl-1-butoxy radicals, bands A and B in the LIF spectra are assigned to origin bands of two different conformers because of the difference in the DF spectra obtained by pumping these two bands. On the contrary, Liang *et al.*²⁹ assigned all vibronic peaks observed in the LIF spectrum of each radical to a single conformer. In their work, A bands were assigned to the $\tilde{B} \leftarrow \tilde{X}$ origin bands of the lowest-energy conformers (the C_1 conformer of isobutoxy and the G_1T_2 conformer of 2-methyl-1-butoxy), while B bands were assigned to transitions to the CO stretch fundamental level of the $\tilde{B}$ state. These assignments were made based on two facts: first, the differences between the $\tilde{B} \leftarrow \tilde{X}$ transition frequencies for the two lowest-energy conformers calculated by the CASSCF method are significantly smaller than the separation between bands A and B. Such a discrepancy, therefore, does not support the assignment of bands A and B to two different conformers. Second, the separations between bands A and B (697 cm^{-1} for isobutoxy and 624 cm^{-1} for 2-methyl-1-butoxy) are close to the calculated excited-state CO stretch frequencies (674 cm^{-1} for isobutoxy and 663 cm^{-1} for 2-methyl-1-butoxy). Although the unambiguous assignment is typically not possible until rotationally resolved LIF spectra are obtained, the experimentally observed DF spectra provide a good foundation for the two-conformer assignment in the present work. We would also like to point out that CASSCF calculations provided extremely accurate predictions of the excited-state CO stretch frequencies for t-butoxy,¹³⁰ 544 cm^{-1} (calculated) vs. 543.9 cm^{-1} (experimental), because this state, unlike the ground electronic ($\tilde{X}^2E$) state, is not subject to strong vibronic interaction. In the present case, the calculated CO stretch frequencies of the isobutoxy and 2-methyl-1-butoxy radicals may not be close enough to the separations between bands A and B, for both radicals, to serve as a strong support to the single-

conformer assignment. Furthermore, prediction of the adiabatic $\tilde{B}-\tilde{X}$ transition frequencies by the CASSCF method might not be accurate enough to guide the conformational assignment because the lower state ($\tilde{X}$) is semi-degenerate with and strongly perturbed by the first excited state ($\tilde{A}$).

Reassignment of B bands from transitions to the CO stretch levels of the lowest-energy conformers to the origin bands of the second-lowest-energy conformers necessitates the reassignment of bands C, D, and E of isobutoxy. As discussed in section 4.1.2, bands C and D in the LIF spectrum are transitions to the same vibrational modes as bands c and d in the DF spectrum, respectively, although their relative frequencies might be slightly different because bands C and D correspond to vibrational modes in the $\tilde{B}$ state while bands c and d correspond to vibrational modes in the $\tilde{X}$ state. In comparison to DFT (for ground state) and CASSCF and CIS (for excited state) calculations, band C (as well as band c) is assigned to the $-\text{CH}_2\text{O}$ wagging mode calculated to be 132 cm^{-1} by the CIS method. Although an antisymmetric mode, this is a pseudo-JT mode that couples the two lowest electronic ($\tilde{A}$ and $\tilde{X}$) states, hence the observation of the LIF transition. Band D (as well as band d) is assigned to the in-phase torsional mode of the two methyl groups calculated to be 254 cm^{-1} . Assignments of the LIF bands are summarized in Table 4.1. A DF spectrum pumping band E ($\tilde{\nu}_E = \tilde{\nu}_B + 428\text{ cm}^{-1}$) was also obtained (Figure 4.12), which suggests that the carrier of band E is formaldehyde. It is well-known that formaldehyde can be generated via β C–C bond fission of highly excited alkoxy radicals produced with 355 nm laser photolysis under jet-cooled conditions.¹³¹

Comparing between the two free radicals investigated in the present work, DF spectra of both conformers of isobutoxy contain sharp lines, while transitions in the DF

spectra of 2-methyl-1-butoxy are broadened. Similarly, lines in the previously reported DF spectra of 2-butoxy were significantly broader than 1-butoxy,³⁴ which was attributed to the smaller $\tilde{A}$ – $\tilde{X}$ separation of 2-butoxy when compared to 1-butoxy, and hence stronger vibronic interaction between the $\tilde{A}$ - and $\tilde{X}$ -states. In the present work, the $\tilde{A}$ – $\tilde{X}$ separation has been determined to be 373 cm^{−1} for the C_I conformer of the isobutoxy radical and 426 cm^{−1} for its C_s conformer, both of which are larger than those of 1-butoxy conformers: 271, 292, and 129 cm^{−1} for its T₁G₂, T₁T₂, G₁T₂ conformers, respectively. $\tilde{B} \rightarrow \tilde{A}$ transitions were not observed in the DF spectra of 2-methyl-1-butoxy probably because its $\tilde{A}$ – $\tilde{X}$ separation is smaller than the experimental resolution, which implies that its $\tilde{A}$ – $\tilde{X}$ separation is even smaller than that of the 2-butoxy radical (55 cm^{−1} for its T conformer). The addition of a methyl group to the isobutoxy radical, therefore, significantly reduces the energy separation and enhances vibronic interaction between the $\tilde{X}$ and $\tilde{A}$ states, which are characterized by different half-filled p π orbitals (p_x and p_y). The present results, therefore, support the hypothesis that line broadening in the DF spectra of alkoxy radicals is at least partially due to vibronic interaction between the nearly degenerate $\tilde{X}$ and $\tilde{A}$ states. DF spectra of both conformers of isobutoxy are simpler when compared to those of t-butoxy,¹²⁰ which contain not only progressions of the CO stretch and its combination bands but also transitions to asymmetric vibrational levels that are usually forbidden by symmetry and allowed in the DF spectra of t-butoxy because of the JT effect. Recent high-resolution spectroscopy investigations revealed both similarities and differences between the rotational and fine structure of the JT molecules (e.g., t-butoxy) and pseudo-JT molecules (e.g., isobutoxy).^{33, 132} It would be interesting to compare the vibronic structures of these two types of molecules. Such investigation, however, is out of the scope of the present

dissertation.

4.5 Conclusions

DF spectra of isobutoxy and 2-methyl-1-butoxy radicals were obtained by pumping different vibronic bands in their LIF spectrum. In all cases, the DF spectra are dominated by CO stretch progressions when the origin bands are pumped and by the progression of combination bands of CO stretch and the pumped modes when other non-CO stretch bands are pumped. Simulated spectra using calculated vibrational frequencies and CFCs well reproduced the DF spectra. Differences between DF spectra obtained by pumping different vibronic bands suggest that for both free radicals, at least two lowest-energy conformers are generated by 355 nm photolysis under jet-cooled conditions.

Table 4.1. Vibronic bands in the LIF spectra of isobutoxy and 2-methyl-1-butoxy reported in reference [29] and their assignments based on DF spectra and calculations obtained in the present work.

radical	band	frequency	vibrational interval		assignment
			expt	calcd ^a	
isobutoxy	A	28091	0		$\tilde{\nu}_{00}^{\tilde{B} \leftarrow \tilde{X}}$ of C _s conformer
	B	28787	0		$\tilde{\nu}_{00}^{\tilde{B} \leftarrow \tilde{X}}$ of C ₁ conformer
	C	28917	$\tilde{\nu}_B + 130$	132	–CH ₂ O wagging
	D	29025	$\tilde{\nu}_B + 238$	254	in-phase methyl torsion
	E	29215			^b
2-methyl-1-butoxy	A	28097	0		$\tilde{\nu}_{00}^{\tilde{B} \leftarrow \tilde{X}}$ of T ₁ T ₂ conformer
	B	28271	0		$\tilde{\nu}_{00}^{\tilde{B} \leftarrow \tilde{X}}$ of G ₁ T ₂ conformer

^a Calculated at the CIS/6-31+G(d) level of theory.

^b Transition of formaldehyde.

Table 4.2. Assignment of transitions in the DF spectrum of the C_s conformer of the isobutoxy radical by pumping its origin band A (Figure 4.1).^a

expt	calcd	assignment	$ \langle v' v'' \rangle ^2$
0	0	$0_0^0(\tilde{B} \rightarrow \tilde{X})$	0.0106
222	224	v_{20}	0.0011
270	277	v_{19}	0.0018
426		$0_0^0(\tilde{B} \rightarrow \tilde{A})$	
601			
651			
824	783	v_{16}	
940	943	v_{15}	0.0039
1010	1044	v_{14}	0.0163
1078	1123	v_{13}	0.0100
2025	2089	$2v_{14}$	0.0133
2100	2168	$v_{14}+v_{13}$	0.0165
2169	2247	$2v_{13}$	0.0047
3021	3134	$3v_{14}$	0.0076
3110	3213	$2v_{14}+v_{13}$	0.0144
3188	3290	$v_{14}+2v_{13}$	0.0082
3271	3370	$3v_{13}$	0.0014
4038	4177	$4v_{14}$	0.0035
4122	4256	$3v_{14}+v_{13}$	0.0088
4197	4335	$2v_{14}+2v_{13}$	0.0077
4283	4414	$v_{14}+3v_{13}$	0.0027
4365	4493	$4v_{14}$	0.0003

^a Experimentally obtained vibrational intervals are compared to calculated $\tilde{X}$ -state vibrational frequencies (in cm^{-1}). Vibrational modes are numbered following the Herzberg convention. FCFs for the $\tilde{B} \rightarrow \tilde{X}$ transitions are calculated using the ezSpectrum software with a threshold of 0.0001.

Table 4.3. Assignment of transitions in the DF spectrum of the C_I conformer of the isobutoxy radical by pumping its origin band B (Figure 4.1).

expt	calcd	assignment	$ \langle v' v'' \rangle ^2$
0	0	$0_0^0 (\tilde{B} \rightarrow \tilde{X})$	0.0144
370		$0_0^0 (\tilde{B} \rightarrow \tilde{A})$	0.0006
421			
712			
1049	1073	v_{23}	0.0398
2082	2145	$2v_{23}$	0.0582
3114	3218	$3v_{23}$	0.0596
4132	4291	$4v_{23}$	0.0481
5133			

Table 4.4. Assignment of transitions in the DF spectrum of the T₁T₂ conformer of the 2-methyl-1-butoxy radical by pumping its origin band A (Figure 4.4).

expt	calcd	assignment	$ \langle v' v''\rangle ^2$
0	0	0 ₀ ⁰	0.0133
1017	1037	v ₃₀	0.0089
1078	1082	v ₂₈	0.0266
1718			
	2074	v ₃₀	0.0028
2114 ^a	2120	v ₃₀ +v ₂₈	0.0189
	2166	v ₂₈	0.0280
2404			
2728			
3110 ^a	3112	2v ₃₀	0.0006
	3157	v ₃₀ +v ₂₈	0.0064
	3203	v ₃₀ +v ₂₈	0.0210
	3248	3v ₂₈	0.0204
3738			
	4194	3v ₃₀ +v ₂₈	0.0014
4257 ^a	4240	2v ₃₀ +2v ₂₈	0.0075
	4285	v ₃₀ +3v ₂₈	0.0161
	4330	4v ₂₈	0.0116
5292 ^a			

^a Center frequency of partially resolved peaks.

Table 4.5. Assignment of transitions in the DF spectrum of the G₁T₂ conformer of the 2-methyl-1-butoxy radical by pumping its origin band B (Figure 4.4).

expt	calcd	assignment	$ \langle v' v'' \rangle ^2$
0	0	0 ₀ ⁰	0.0133
1045 1323	1074	v ₂₈	0.0367
2085 2356	2147	2v ₂₈	0.0538
3106 3369	3220	3v ₂₈	0.0554
4131 4381 5157 5371	4294	4v ₂₈	0.0450

Table 4.6. Experimentally determined ground-state vibrational energy levels $G(v)$ of the CO stretch progression (in cm^{-1}) of the C_I conformer of the isobutoxy radical. $\Delta G(v) = G(v) - G(v-1)$.

v	$G(v)$	$\Delta G(v)$
0	0	
1	1049	1049
2	2082	1033
3	3114	1032
4	4132	1018
5	5133	1001

Table 4.7. Experimentally determined ground-state vibrational energy levels $G(v)$ of the CO stretch progression (in cm^{-1}) of G_1T_2 conformer of the 2-methyl-1-butoxy radical.

v	$G(v)$	$\Delta G(v)$
0	0	
1	1045	1045
2	2088	1043
3	3135	1047
4	4149	1014

Figure 4.1. DF spectra of the isobutoxy radical. The asterisked peak is due to scattering of the 355 nm photolysis laser. Numbers in parentheses are LIF excitation frequencies.

Figure 4.2. Comparison between the simulated DF spectra of the C_s and C_l conformers of the isobutoxy radical (blue) and the experimentally obtained ones by pumping bands A and B in the LIF spectrum (red).

Figure 4.3. DF spectra of the isobutoxy radical obtained by pumping LIF bands B–D. The spectra obtained by pumping vibronic bands other than the origin (band B) are blue-shifted by the $\tilde{X}$ -state vibrational frequency of the pumped mode so that the DF bands to the $\tilde{X}$ -state vibrational levels are aligned.

Figure 4.4. DF spectra of 2-methyl-1-butoxy radical (red) compared with simulation (blue). The asterisked peak is due to scattering of the 355 nm photolysis laser.

**Pumped
LIF Bands:**

Figure 4.5. Comparison between the second members of the CO-stretch progression in the DF spectra of the isobutoxy radical by pumping Bands A and B in the LIF spectrum. Difference in transition frequencies of the observed DF peaks supports a two-conformer assignment.

Figure 4.6. Determination of the harmonic frequency (ω_e) and the anharmonic parameter ($\omega_e\chi_e$) of the $\tilde{X}$ -state CO stretch of the C_I conformer of isobutoxy. $G(v)$ is the vibrational energy of the v^{th} member of the CO-stretch progression.

Figure 4.7. Vibrational modes of the C_1 conformer of isobutoxy. a) $-\text{CH}_2\text{O}$ wagging mode (ν_{36}), to which Bands C (in the LIF spectrum) and c (in the DF spectra) are assigned. b) in-phase CH_3 torsional mode (ν_{34}), to which Bands D (in the LIF spectrum) and d (in the DF spectra) are assigned. In parentheses are calculated vibrational frequencies in cm^{-1} . Unprimed and primed labels are used to denote the $\tilde{X}$ - and $\tilde{B}$ -state vibrational modes, respectively.

Figure 4.8. $\tilde{X}$ -state vibrational modes of the C_s conformer of isobutoxy. a) ν_{16} (umbrella mode), b) ν_{15} (mixture of CH_3 scissoring and C-C stretch modes), c) ν_{14} , and d) ν_{13} . ν_{14} and ν_{13} are mixtures of CO stretch and the umbrella modes.

Figure 4.9. Determination of the harmonic frequency (ω_e) and the anharmonic parameter ($\omega_e\chi_e$) of the $\tilde{X}$ -state CO-stretch of the G₁T₂ conformer of 2-methyl-1-butoxy.

Figure 4.10. $\tilde{X}$ -state vibrational modes of the T_1T_2 conformer of 2-methyl-1-butoxy. a) ν_{43} (C-C-C bending mode), b) ν_{30} , and c) ν_{28} . ν_{30} and ν_{28} are mixtures of CO-stretch and the C-C stretch modes.

Figure 3.11 $\tilde{X}$ -state vibrational modes of the G_1T_2 conformer of 2-methyl-1-butoxy radical. a) ν_{43} (C₃-position methyl torsional mode), b) ν_{42} (C₄-position methyl torsional mode) and c) ν_{28} (CO-stretch mode).

Figure 4.12. DF spectra of the isobutoxy radical by pumping Band E in its LIF spectrum, which suggests that the molecular carrier of Band E is formaldehyde.

CHAPTER V

LASER-INDUCED FLUORESCENCE AND DISPERSED FLUORESCENCE

SPECTROSCOPY OF JET-COOLED ISOPENTHOXY RADICALS

5.1 Introduction

Alkoxy radicals are formed in high yields during the oxidation of hydrocarbons. They play key roles as reaction intermediates in low-temperature combustion,^{3, 133} and the atmosphere, especially the troposphere.^{1, 2} They have been studied by laser-induced fluorescence (LIF),^{28, 84, 134} dispersed fluorescence (DF),^{34, 93} and other laser-spectroscopy techniques. These spectroscopic investigations have furnished an understanding of the molecular structure and properties of alkoxy radicals and provided useful information for molecular dynamics and chemical reaction kinetic studies in which these important free radicals are involved. Such information includes origin frequencies, vibrational and rotational structure, and excited-state lifetimes. The atmospheric chemistry of large alkoxy radicals (with more than four carbons) is dominated by three main chemical reactions: reaction with O₂, unimolecular dissociation *via* C–C bond fission, and isomerization through H-shift. These reactions can be highly sensitive to molecular structure.⁶ Conformation-specific spectroscopy investigations are, therefore, critical to the study of alkoxy radicals.

Here we report LIF and DF spectra of one particular isomer of the pentoxy radicals, namely, 3-methyl-1-butoxy [(CH₃)₂CHCH₂CH₂O], also known as the isopentoxy radical. Among all pentoxy isomers, isopentoxy is especially interesting in dynamics studies because of its β C–C bond fission, which is affected strongly by its conformation.

Previously, the vibrationally resolved LIF spectrum of isopentoxy radicals produced in a supersonic jet expansion was reported by Liang *et. al.*²⁹ However, no conformational or vibrational assignment was made because of the lack of clear vibrational progressions. In the present work, we report a new LIF measurement of the isopentoxy radical, in which more vibronic bands were observed owing to optimized experimental conditions and increased signal-to-noise ratio. In addition, DF spectra have been obtained by pumping different vibronic transitions in the LIF spectrum. Similarities between the DF spectra allow the differentiation of conformational carriers of the vibronic bands in the LIF spectrum. Both the conformational identification and the vibrational assignments are aided by simulations using newly calculated adiabatic electronic transition frequencies, vibrational frequencies of the ground and excited states, and the Franck-Condon factors (FCFs) of the vibronic transitions.

5.2 Calculations

5.2.1 Potential energy surface (PES) scan and conformational search

Conformers of isopentoxy are defined with two dihedral angles: Φ_1 : OC₁C₂C₃ and Φ_2 : C₁C₂C₃H. Each dihedral angle can have three orientations in stable conformers: trans (T, $\Phi \approx 180^\circ$), counterclockwise gauche (G, $\Phi \approx 60^\circ$), and clockwise gauche (G', $\Phi \approx -60^\circ$). Internal rotation of the methyl groups does not introduce new stable conformations.

Therefore, there are $3 \times 3 = 9$ conformers, 5 of which are optically distinguishable: TT, TG (TG'), GT (G'T), GG (G'G'), and GG' (G'G). (In parentheses are enantiomers.) Geometry optimization confirms that all five conformations are stable structures (see below). These five conformers are depicted in Figure 5.1.

5.2.2 Quantum Chemical Calculations

Significant computational work on isopentoxo has been done at the B3LYP/6-311++G(d,p) level of theory by Liang *et al.*²⁹ No simulation of the $\tilde{B} \leftrightarrow \tilde{X}$ transitions was reported. In the present work, it has been found that accurate prediction of the $\tilde{B} \leftrightarrow \tilde{X}$ transition frequencies and, in most cases, satisfactory simulation of the LIF spectra of conformers can be achieved by including long-range corrections (see Section 5.3). The Coulomb-attenuating method CAM-B3LYP functional¹¹² was adopted for the calculation of both ground and excited electronic states. All calculations presented here were done at the CAM-B3LYP/6-311+G(d) (for the $\tilde{B}$ -state) or time-dependent (TD-) CAM-B3LYP/6-311+G(d) for the $\tilde{B}$ -state level of theory using the *Gaussian 09* software package.¹¹⁴

Of all the geometric parameters, the $\tilde{B} \leftarrow \tilde{X}$ excitation affects the CO bond length, the OC₁C₂ angle, and the two dihedral angles (Φ_1 and Φ_2) most significantly because the excitation corresponds to an electron promotion from the $p\sigma_z$ to the $p\pi_x$ or $p\pi_y$ orbital of the oxygen atom. The optimized values of these geometric parameters for both the $\tilde{X}$ and $\tilde{B}$ states of all five conformers are summarized in Table 5.1. It is important to point out that the long-range Coulombic interaction between oxygen and the tertiary hydrogen leads to the large change of Φ_1 and Φ_2 upon the $\tilde{B} \leftarrow \tilde{X}$ excitation for the GG, GG' and GT ($\Phi_1 = \text{G}$)

conformers. For the TG conformer, the change of Φ_1 and Φ_2 is insignificant because of the larger distance between the oxygen and tertiary hydrogen atoms (see Figure 5.1).

Calculated relative energies of isopentoxy conformers, the adiabatic excitation frequencies of their $\tilde{B} \leftarrow \tilde{X}$ transitions, as well as the $\tilde{X}$ - and $\tilde{B}$ -state CO stretch frequencies are listed in Table 5.2. Calculations show that three of the five conformers: GG', TG, and GG (referred to as Conformers 1, 2, and 4 in ref.,²⁹ respectively) are close in energy (<0.3 kcal/mol), while the other two are significantly higher in energy (>1 kcal/mol). Therefore, only the three lowest-energy conformers are expected to have detectable concentrations in the supersonic jet expansion. FCFs for $\tilde{B} \leftarrow \tilde{X}$ ($v''=0$) transitions of these three conformers were calculated using the ezSpectrum program.¹²¹ Due to the large difference in $\tilde{X}$ - and $\tilde{B}$ -state geometries (Table 5.1), Duschinsky rotations were taken into account in the calculation of FCFs to better reproduce the experimental spectrum.^{122, 123} Experimentally obtained LIF and DF spectra are simulated using calculated vibrational frequencies and FCFs (see below).

5.3 Results

5.3.1 Overview of LIF and DF Spectra

Figure 5.2a shows the vibrationally resolved LIF spectrum of the $\tilde{B} \leftarrow \tilde{X}$ transition of isopentoxy. It lacks the CO-stretch progressions that are typical in the LIF spectra of alkoxy radicals. Nevertheless, two vibrational progressions with different origins have been observed in the low-frequency region. They are color-coded and labeled A₀, A₁, A₂ ... and B₀, B₁, B₂ ... in Figure 5.2a. Harmonic frequencies and anharmonic parameters of these

two vibrational progressions were determined by fitting Birge-Sponer plots (Figure 5.5). For Progression A, $\omega_e = 77.0 \pm 1.5 \text{ cm}^{-1}$ and $\omega_e\chi_e = 2.1 \pm 0.3 \text{ cm}^{-1}$, while for Progression B, $\omega_e = 49.1 \pm 0.6 \text{ cm}^{-1}$ and $\omega_e\chi_e = 0.5 \pm 0.1 \text{ cm}^{-1}$. Strong peaks in the higher-frequency region of the LIF spectrum are labeled Bands C through L. They do not show any obvious pattern.

To help differentiate vibronic bands in the LIF spectrum by their molecular carriers, the DF spectra of isopentoxo were recorded by pumping different vibronic bands in the LIF spectrum. DF spectra obtained by pumping the A Bands do not contain any peaks other than the strong zero-redshift transition. Figure 5.6 shows an exemplary DF spectrum obtained by pumping Band A₂.

DF spectra obtained by pumping the B Bands have similar vibronic structures, although they are shifted from each other (Figure 5.3). In all cases, a vibrational progression of $\sim 1025 \text{ cm}^{-1}$ is discernable despite the broad linewidth of its members. The first two members of the progression are too weak to be detected. By extrapolation, the origin of the vibrational progression in the DF spectrum obtained by pumping each B Band can be determined. It is 409 cm^{-1} when Band B₀ is pumped.

DF spectra obtained by pumping Bands C-L (Figure 5.4) contain two strong vibrational progressions, both of which have frequency intervals of $\sim 1045 \text{ cm}^{-1}$. When Band C or L is pumped, one of the progressions starts from zero red-shift, while the other starts with a weak peak at 263 cm^{-1} (labeled “X” in Figure 5.4a). DF spectra obtained by pumping Band D-K are similar, except that the two vibrational progressions are red-shifted.

On the basis of the similarities and differences of the DF spectra, we attribute the three groups of LIF bands (the A Band, the B Bands, and Bands C-L) to three molecular carriers, namely, the three lowest-energy conformers of the isopentoxy radical. Bands A₀ (28598 cm⁻¹), B₀ (28821 cm⁻¹), and C (29058 cm⁻¹) are assigned to the origin bands. The cause of the red-shift in the DF spectra within each group has been discussed in our previous publications.^{35, 93, 96} In brief, the large change in the CO bond length upon the $\tilde{B} \leftarrow \tilde{X}$ transition of alkoxy radicals leads to Duschinsky mixing^{122, 123} between the CO-stretch mode and other vibrational modes. Consequently, when the free radical is excited to non-CO-stretch vibrational levels of the $\tilde{B}$ -state, DF emission to combination levels of the CO stretch and the pumped vibrational mode are FC-favored. If the DF spectra are blue-shifted by the ground-state frequencies of the non-CO-stretch levels, the strong peaks will be lined up. (See Figures 5.8 and 5.9) The DF spectrum obtained by pumping Band L is not red-shifted to that obtained by pumping Band C, an origin band. Therefore, Band L (663 cm⁻¹ with respect to Band C) is assigned to the CO-stretch band.

5.3.2 Simulation, Conformational Identification, and Vibrational Assignment of LIF Spectrum

The calculated origin band frequencies of the three lowest-energy conformers of isopentoxy are 29650 cm⁻¹ for GG', 29780 cm⁻¹ for GG, and 30036 cm⁻¹ for TG. In comparison, transition frequencies for Band A₀, B₀, and C are 28598, 28821, and 29058 cm⁻¹, respectively. When a scaling factor of 0.967 is applied, the calculated origin-band frequencies reproduce the experimental ones quite well (see the 6th and 7th Columns of Table 5.2). The simulated LIF spectra of the GG', GG, and TG conformers are compared

with the experimental LIF spectrum in Figures 5.2b-d, in which the calculated origin bands are shifted to match Bands A₀, B₀, and C, respectively.

The simulated LIF spectrum of the TG conformer (Figure 5.2b) reproduces the relative frequencies and intensities of most strong peaks in the higher-frequency region of the experimental LIF spectrum (Figure 5.2a) quite well. Comparing the relative frequencies of Bands C-L to the calculated vibrational frequencies of the $\tilde{B}$ -state TG conformer, we are able to assign these vibronic bands, which confirms the assignment of Bands C-L to the TG conformer. The vibrational assignment is summarized in Table 5.3. The simulated LIF spectrum of the GG conformers contains a vibrational progression of 56 cm⁻¹ in the low-frequency region (labeled B₀, B₁, B₂... in Figure 5.2c). These are transitions to the vibrational levels of the C₁C₂C₃H torsion mode.

In comparison, the progression of B Bands in the experimental LIF spectrum has a harmonic frequency of $\omega_e=49.1\pm0.6$ cm⁻¹. It is, therefore, reasonable to assign the B Bands to the GG conformer. The simulated LIF spectrum of the GG' conformer (Figure 5.2d) does not contain a progression of the lowest-frequency C₁C₂C₃H torsion mode (calculated to be 66 cm⁻¹). Instead, only the transition to its fundamental level has significant intensity (labeled A₁ in Figure 5.2d). Instead, transitions to several low-frequency vibrational modes and their combination bands are predicted.

Nevertheless, we assign the A Bands in the experimental LIF spectrum to this conformer based on two facts. First, the calculated (and scaled) origin transition of the GG' conformer matches the frequency of the A₀ band. Second, the GG' conformer is the lowest-energy conformer and is expected to be present under jet-cooled conditions. Bands A₀, B₀,

and C are the origin bands of the GG', TG, and GG conformers, respectively. Discrepancies between the simulated and experimental spectra will be discussed in Section 5.4.

5.3.3 DF Spectra Obtained by Pumping the Origin Bands

Simulation of DF spectra of isopentoxo was not attempted for two reasons: (i) severe broadening of transitions in the DF spectra, and (ii) the expected complexity of the vibronic structure of the quasi-degenerate $\tilde{X}$ - and $\tilde{A}$ - states. In a CAM-B3LYP calculation in which the HUMO and LUMO of the β electron are swapped,¹³² the energy separation between the $\tilde{X}^2A''$ and the low-lying $\tilde{A}^2A'$ states of the TT (C_s) conformer of isopentoxo was determined to be 208 cm⁻¹. $\tilde{A}$ – $\tilde{X}$ separations of other conformers, which have C_1 symmetry, cannot be calculated accurately but are expected to be comparable to that of the TT conformer. Due to the small $\tilde{A}$ – $\tilde{X}$ separations, strong pseudo-Jahn-Teller and spin-orbit interactions between these two states are expected, which causes complicated vibronic structure. The broadening of the DF transitions may be attributed to both the complicated vibronic structure and the low isomerization barriers between conformers. (See Figure 5.10.)

Nevertheless, we may tentatively assign dominant features in the DF spectra according to quantum chemical calculations. In the DF spectrum obtained by pumping Band B₀, the origin band of the GG conformer, the broad vibrational progression of ~1025 cm⁻¹ is assigned to CO-stretch bands of the $\tilde{B} \rightarrow \tilde{A}$ transition of conformer GG. The CAM-B3LYP calculation predicts several $\tilde{X}$ -state modes that have CO-stretch character with frequencies of 1008, 1091, and 1111 cm⁻¹. Similar CO-stretch modes are expected for the $\tilde{A}$ state. The existence of multiple vibrational modes with CO-stretch character may explain the unusually broad linewidths of features in the DF spectrum. The vibrational progression

starts at $\sim 409\text{ cm}^{-1}$, which is attributed to the $\tilde{A}-\tilde{X}$ separation. The $\tilde{B} \rightarrow \tilde{X}$ transitions may be obscured by strong $\tilde{B} \rightarrow \tilde{A}$ transitions, although this cannot be confirmed from the present DF spectrum.

Similarly, the two $\sim 1045\text{ cm}^{-1}$ vibrational progressions in the DF spectrum obtained by pumping Band C, the origin band of the TG conformer, are assigned to CO-stretch bands of the $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ transitions of TG. This should be compared to the calculated $\tilde{X}$ -state CO-stretch mode of 1096 cm^{-1} , with another vibrational mode of 1037 cm^{-1} that has a CO-stretch character. The separation between the two vibrational progressions (263 cm^{-1}) is attributed to the $\tilde{A}-\tilde{X}$ separation,

5.4 Discussion

Although quantum chemical calculations predict strong features in the LIF spectra of the GG' and GG conformers (Figure 5.2c and 5.2d), they are absent in the experimental spectrum (Figure 5.2a). Only two very weak low-frequency vibrational progressions (the A Bands and B Bands) are present in the low-frequency region. Similarly, for the TG conformer, although the calculation predicts a CO-stretch band (at 691 cm^{-1} relative to the origin band) that is significantly stronger than the origin band (Figure 5.2b), it is significantly weaker than the origin band in the experimental spectrum (Figure 5.2a). The discrepancy between the experimental and predicted transition intensities may be attributed to either $\tilde{B}$ -state β C–C fission or pre-dissociation of the $\tilde{B}$ state *via* the CO bond breaking by highly excited electronic states.¹³⁵ The latter mechanism is a more plausible explanation based on both calculations and experimental evidence. The barrier for ground-state β C–C fission was calculated to be 12.9 kcal/mol (4512 cm^{-1}).²⁹ Experimentally, transitions of

formaldehyde, one of the products of β C–C fission was observed in our LIF experiment (see Figure 5.11), which confirms the low barrier. Although a TD-CAM-B3LYP calculation of the barrier for $\tilde{B}$ -state β C–C fission was not successful, the barrier is expected to be lower than the ground state because in the $\tilde{B}$ -state the half-filled $2p\sigma$ orbital of the CO bond further weakens the adjacent C–C bond.

The two low-frequency vibrational progressions in the experimental LIF spectrum are assigned to GG and GG' conformers. They correspond to the lowest-frequency vibrational modes of these two conformers, which involve the torsion of the Φ_2 ($C_1C_2C_3H$) dihedral angle. For the GG conformer, the CAM-B3LYP calculation predicts a very large change of Φ_2 upon $\tilde{B} \leftarrow \tilde{X}$ excitation (from 56° to 33°). Hence, the simulated LIF spectrum of this conformer contains a long vibrational progression of this mode. For the GG' conformer, the change of Φ_2 (from -52° to -65°), although still significant, is much smaller than for the GG conformer. The predicted LIF spectrum of this conformer, therefore, does not contain a low-frequency vibrational progression, whereas the experimental LIF spectrum does. Therefore, we suspect that the CAM-B3LYP calculation underestimates the Φ_2 dihedral angle of GG' in its $\tilde{B}$ state. Calculations using other density-functional methods with long-range corrections, including wB97XD, have been employed¹³⁶ to optimize the $\tilde{B}$ -state geometries of isopentoxo conformers. The results are close to those using CAM-B3LYP. Further computational investigation using other methods is therefore necessary to reproduce the experimentally obtained LIF spectrum.

5.5 Conclusions

We have observed $\tilde{B}-\tilde{X}$ LIF and DF spectra of jet-cooled isopentoxo radicals. Of all five conformers (GG', TG, GG, TT, and GT), the three lowest-energy ones (GG', TG, and GG) are identified as spectral carriers based on vibronic simulations. LIF spectra of GG' and GG conformers contain low-frequency vibrational progressions due to large changes of the $C_1C_2C_3H$ dihedral angle between the $\tilde{B}$ - and $\tilde{X}$ -states. Most experimentally observed LIF transitions are reproduced in simulations using electronic transition frequencies, vibrational frequencies, and Franck-Condon factors calculated at the CAM-B3LYP/6-311+G(d) level of theory. The absence of strong transitions to the CO-stretch levels is attributed to low-barriers for β C–C fission or predissociation in the $\tilde{B}$ -state. DF spectra of the GG and TG conformers are dominated by strong vibrational progressions of the CO-stretch mode or its combination with other vibrational modes due to Duschinsky mixing. The $\tilde{A}-\tilde{X}$ separations of the GG and TG conformers have been determined to be 409 and 263 cm^{-1} , respectively.

Table 5.1. Geometric parameters of conformers of the isopentoxy radical in the $\tilde{X}$ - and $\tilde{B}$ -states calculated at the CAM-B3LYP/6-311+G(d) level of theory.

conformer	C-O (Å)		$\angle$ OCC (deg.)		$\Phi_1\text{OC}_1\text{C}_2\text{C}_3$ (deg.)		$\Phi_2\text{C}_1\text{C}_2\text{C}_3\text{H}$ (deg.)	
	$\tilde{X}$	$\tilde{B}$	$\tilde{X}$	$\tilde{B}$	$\tilde{X}$	$\tilde{B}$	$\tilde{X}$	$\tilde{B}$
GG'	1.36	1.58	116	107	61	57	-52	-65
TG	1.36	1.59	115	107	177	175	56	57
GG	1.36	1.59	116	109	75	65	56	33
TT	1.36	1.6	115	107	178	180	179	180
GT	1.36	1.59	115	109	72	63	179	158

Table 5.2. Numbers of enantiomers calculated relative energies, adiabatic excitation energies ($\Delta E^{\tilde{B}-\tilde{X}}$) and oscillator strengths (f) of the $\tilde{B}-\tilde{X}$ transition, and $\tilde{X}$ - and $\tilde{B}$ -state CO-stretch frequencies ($\nu_{CO}^{\tilde{X}}$ and $\nu_{CO}^{\tilde{B}}$) of isopentoxo conformers. $\Delta E^{\tilde{B}-\tilde{X}}$ includes zero-point-energy corrections. Note that for the TG and GG conformers, there are more than one vibrational mode with the CO-stretch character.

conformer	No. of enantiomers	relative energy (cm^{-1})	oscillator strength		$\Delta E^{\tilde{B}-\tilde{X}}$		$\tilde{X}$ ν_{CO} (cm^{-1})	$\tilde{B}$ ν_{CO} (cm^{-1})
			$f \times 10^4$	cal'd	scaled ^a	Expt.		
GG'	2	0	2.84	29650	28671	28598	1101	620
TG	2	262	2.86	30036	29044	28821	1037, 1096	691
GG	2	291	8.49	29780	28798	29058	1008, 1091, 1111	607
TT	1	616	1.98	29771	28789		1084	697
GT	2	667	6.43	29626	28649		1084	612

^aScaling factor = 0.967.

Table 5.3. Experimental and calculated vibrational frequencies (in cm^{-1}) and assignment of vibronic bands in the LIF spectra (Figure 4.2a).

Conformer	Band	Expt. ^a	Cal'd ^b	Assignment ^c
GG'	A ₀	0	0	$\tilde{\nu}_{00}^{\tilde{B} \leftarrow \tilde{X}}$
	A ₁	73	66	ν_{45}
	A ₂	142	128	ν_{44}
	A ₃	205	216	ν_{43}
	A ₄	266	286	ν_{41}
GG	B ₀	0	0	$\tilde{\nu}_{00}^{\tilde{B} \leftarrow \tilde{X}}$
	B ₁	48	56	ν_{45}
	B ₂	95	113	$2\nu_{45}$
	B ₃	142	169	$3\nu_{45}$
	B ₄	188	225	$4\nu_{45}$
	B ₅	232	275	$\nu_{45} + \nu_{44}$
TG	C	0	0	$\tilde{\nu}_{00}^{\tilde{B} \leftarrow \tilde{X}}$
	D	68		
	E	133	105	ν_{44}
		167	161	$2\nu_{45}$
	F	177	179	ν_{43}
		205		
	G	224	235	ν_{42}
	H	310	320	ν_{40}
	I	354	357	$2\nu_{43}$
		411	413	$\nu_{43} + \nu_{42}$
	J	417	426	ν_{38}
		487	499	$\nu_{43} + \nu_{40}$
	K	508		
	L	663	691	ν_{36}

^a Observed band maximum (cm^{-1}) relative to the origin band ($\tilde{\nu}_{00}^{\tilde{B} \leftarrow \tilde{X}}$) at 28598 cm^{-1} (A₀), 28821 cm^{-1} (B₀), and 29058 cm^{-1} (C) for the GG', GG, and TG conformer, respectively.

^b Unscaled $\tilde{B}$ -state vibrational frequencies calculated at the CAM-B3LYP/6-311+G(d) level of theory.

^c Vibrational modes are numbered following the Herzberg convention. ν_{45} : C₁C₂C₃H torsion. ν_{36} of TG: CO stretch.

Figure 5.1. The five conformers of isopentoxy and their relative energies (cm^{-1}).

Figure 5.2. (a) Vibrationally resolved LIF spectrum of isopentoxy. (b-d) Simulated LIF spectra of the GG' (b), GG (c) and TG (d) conformers. The asterisked band is due to CH_2O .

Pumped LIF Bands:

Figure 5.3. DF spectra of the isopentoxy radical obtained by pumping LIF bands B₀-B₄. Numbers in parentheses after the pumped LIF bands are relative wavenumbers with respect to the origin band (Band B₀). The asterisked bands are due to photolysis laser scattering.

Pumped LIF Bands:

Figure 5.4. DF spectra of the isopentoxo radical obtained by pumping LIF bands C-L. Numbers in parentheses after the pumped LIF bands are relative wavenumbers with respect to the origin band (Band C). The asterisked bands are due to photolysis laser scattering.

Figure 5.5. Birge-Sponer plot of the "A" Bands in the LIF spectrum of isopentoxy.

Figure 5.6. Birge-Sponer plot of the "B" Bands in the LIF spectrum of isopentoxy.

Figure 5.7. DF spectrum of the isopentoxy radical obtained by pumping LIF bands A_2 . Numbers in parentheses after the pumped LIF bands are relative wavenumbers with respect to the origin band (Band A_0). The asterisked band is due to photolysis laser scattering.

Pumped LIF Bands:

Figure 5.8. DF spectra of the isopentoxo radical obtained by pumping LIF bands B₀-B₄. The DF spectra are blue-shifted by ground-state vibrational frequencies of the pumped modes. Numbers in parentheses after the pumped LIF bands are relative wavenumbers with respect to the origin band (Band B₀). The asterisked band is due to photolysis laser scattering.

Figure 5.9. DF spectra of the isopentoxy radical obtained by pumping LIF bands C-L. The DF spectra except that obtained by pumping the CO stretch band (Band L) are blue-shifted by ground-state vibrational frequencies of the pumped modes. Numbers in parentheses after the pumped LIF bands are relative wavenumbers with respect to the origin band (Band C). The asterisked band is due to photolysis laser scattering.

Figure 5.10. Scans of $\tilde{X}$ - and $\tilde{B}$ -state potential energy surfaces of the isopentoxy radical along the coordinates of the OC₁C₂C₃ and C₁C₂C₃H dihedral angles.

Figure 5.11. LIF spectrum that contains transitions of formaldehyde, a product of β C-C fission of isopentoxy.

CHAPTER VI

DISPERSED FLUORESCENCE SPECTROSCOPY OF JET-COOLED 2-, 3-, AND 4-METHYLCYCLOHEXOXY RADICALS

6.1 Introduction

The cyclohexoxy radical, like other alkoxy radicals, is an important reaction intermediate in combustion and atmospheric chemistry.^{1, 2, 4, 9, 94} The stability of the six-membered ring and its complicated conformational behavior³² makes cyclohexoxy particularly interesting in all cyclic alkoxy radicals. From the point of view of theoretical spectroscopy, cyclohexoxy, as well as other cyclic alkoxy radicals, is a prototypical pseudo-Jahn–Teller (pJT) molecule.^{33, 35, 137} Its two lowest electronic states ($\tilde{X}$ and $\tilde{A}$) are separated by only 61 cm^{-1} in energy from each other.^{33, 35} Analysis of the rotational and fine structure of the $\tilde{X} / \tilde{A}$ state decomposes the $\tilde{A} - \tilde{X}$ separation into two components: the spin–orbit (SO) splitting and the nonrelativistic separation because of difference in both the electrostatic energy and the zero-point energy (ZPE) between the two states.^{33, 132}

It is of both theoretical and practical interests to extend the spectroscopic investigation of cyclohexoxy to the methylcyclohexoxy (MCHO) radicals. Especially important is the effect of the methyl group position at the six-membered ring. Previously,

the $\tilde{B} \leftarrow \tilde{X}$ transitions of all four isomers of MCHO were studied in laser-induced fluorescence (LIF) spectroscopy under jet-cooled conditions.^{36, 37} Both the origin band frequencies and vibronic structures of these isomers are different from each other. Such observation confirms the effect of methyl substitution on the $\tilde{B}$ state vibrational structure.

Intramolecular dynamics and chemical kinetics of MCHOs, and indeed alkoxy radicals in general, are also affected by the lowest-energy electronic states ($\tilde{X}$ and $\tilde{A}$). Because all alkoxy radicals can be treated as the alkyl substitution of the methoxy radical (CH_3O), these two states are originated from the $\tilde{X}^2\text{E}$ state of CH_3O , which is orbitally doubly degenerate. The unpaired electron may occupy either of the two nonbonding orbitals resulting from the p_x and p_y orbitals of the oxygen atom, which lie within the OCH plane and perpendicular to it, respectively. In larger alkoxy radicals such as ethoxy,²⁴ all-trans conformers of large primary alkoxies,^{134, 135, 138} isopropoxy,^{26, 132} and cyclohexoxy,^{33, 35} the alkyl substitution reduces the molecular symmetry from C_{3v} (for methoxy) to C_s and removes the orbital degeneracy. The $\tilde{X}^2\text{E}$ state of the methoxy radical therefore splits into two close-lying states ($\tilde{X}$ and $\tilde{A}$) with A' and A'' symmetry, which have the half-filled orbital of the oxygen atom within the C_s plane (p_x) and perpendicular to it (p_y), respectively. The alkyl group interacts differently with the p_x and p_y orbitals, resulting in the $\tilde{A}$ – $\tilde{X}$ separation between the lowest vibrational levels of these two states. The mechanism of interaction between these two close-lying states is of significant theoretical importance.^{137, 139, 140} Especially, the energy ordering of the A' and A'' states and the magnitude of the $\tilde{A}$ – $\tilde{X}$ separation depend on the conformation of the free radicals. For gauche conformers of the primary alkoxy radicals^{88, 134, 138} and secondary alkoxy radicals larger than isopropoxy,¹⁴¹

the molecular symmetry is further lowered to C_1 . $\tilde{A}$ - $\tilde{X}$ separation of conformers with C_1 symmetry of an alkoxy radical is usually smaller than that of C_s conformers.

In addition to the lowest vibrational levels, the vibronic structure of the $\tilde{X}/\tilde{A}$ state can be affected by positional isomerization too. In the present work, we report an investigation of the effect of the methyl group position at the six-membered rings of MCHO radicals by dispersed fluorescence (DF) spectroscopy. Experimental DF spectra obtained by pumping different bands in the $\tilde{B} \leftarrow \tilde{X}$ LIF spectra reveal the $\tilde{A}$ - $\tilde{X}$ separation and vibrational structure of the $\tilde{X}/\tilde{A}$ state. By comparing the experimentally observed redshifts with the calculated vibrational frequencies, the vibronic bands in the DF spectra can be assigned to transitions to different vibrational levels of the lower two states. The transition intensities provide further information about the geometry, symmetry, and energetics of the electronic states. The DF spectra of 1-MCHO are significantly different from those of the others because of its tertiary structure and hence deferred to future publication. In the present paper, the results of 2-, 3-, and 4-MCHOs are reported.

6.2 Quantum Chemical Calculations

Previously, extensive calculations were performed on the $\tilde{X}$ - and $\tilde{B}$ -state 2-, 3-, and 4-MCHO radicals and used to guide the analysis of the experimentally obtained LIF spectra.³⁶ Such analysis allowed the assignment of vibronic bands in the LIF spectra and suggested that all LIF bands observed under jet-cooled conditions are due to the lowest-energy conformers of each isomer. The six-membered ring in these conformers has chair

structure, and both the oxygen atom and the methyl group are at the equatorial positions. In the present work, two types of new calculations have been carried out in aid of the analysis of the DF spectra. First, density functional theory (DFT) calculations at the B3LYP/6-31+G(d) level of theory were performed to predict the energy separation between the $\tilde{X}$ and the $\tilde{A}$ states of 4-MCHO, which retains the C_s symmetry of the cyclohexoxy radical. This was done by putting the unpaired electron in either p_x or p_y orbitals localized on the oxygen atom. The calculations predict that the ground electronic state ($\tilde{X}$) has A'' symmetry, whereas the first excited state ($\tilde{A}$) is of A' symmetry. The energy separation between these two states was found to be 168 cm^{-1} (without ZPE corrections). When the molecular symmetry was allowed to be lowered to C_1 , geometry optimization resulted in the pJT-distorted structure of the 4-MCHO isomer. The pJT stabilization energy, defined as the energy difference between the ground-state ($\tilde{X}^2A''$) molecule with C_s symmetry and that with C_1 geometry, i.e., no symmetry, was found to be 77 cm^{-1} .

2- and 3-MCHO isomers do not have C_s symmetry. The aforementioned technique, therefore, cannot be used to calculate the $\tilde{A}$ – $\tilde{X}$ separation and the pJT stabilization energy. However, an inspection of the molecular orbitals suggests that for the ground electronic state of both isomers, the half-filled orbital is approximately perpendicular to the OCH plane, viz., the p_y orbital. These isomers, therefore, have a ground state with “pseudo- A'' symmetry.” Figure 6.1 illustrates the half-filled orbitals of 2-, 3-, and 4-MCHOs. All calculations were done using the Gaussssian09 software package.¹²⁸

The second type of new calculations on MCHOs are Franck–Condon factor (FCF) calculations for $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ transitions. Vibrational modes of the $\tilde{A}$ state (for 4-

MCHO only) and the $\tilde{X}$ state were calculated at the B3LYP/6-31+G(d) level of theory, whereas those of the $\tilde{B}$ state by configuration interaction singles (CIS) using the same basis set. For the $\tilde{X}$ state of 4-MCHO, the pJT distorted (C_I) geometry was used. Geometries and the displacements of nuclei for the normal modes were calculated using Gaussian09,¹²⁸ and the FCFs and intensities for transitions from the lowest vibrational level of the $\tilde{B}$ state to the vibrational levels of the $\tilde{X}/\tilde{A}$ state were predicted using the ezSpectrum software.¹²¹ Due to the large difference in $\tilde{X}/\tilde{A}$ - and $\tilde{B}$ -state geometries, especially the large increase in CO bond length upon excitation (e.g., from 1.37 to 1.58 Å for 4-MCHO), the Duschinsky rotations were taken into account in the calculation of FCFs. The calculated vibrational frequencies of the $\tilde{X}/\tilde{A}$ state and $\tilde{B} \rightarrow \tilde{X}/\tilde{A}$ FCFs are listed in Tables 6.4–7.

6.3 Results

DF spectra of 2-, 3-, and 4-MCHOs were obtained by pumping different vibronic bands of the $\tilde{B} \leftarrow \tilde{X}$ LIF excitation spectra.³⁶ The vibronic bands are labeled by capitalized letters following ref.³⁶ In this section; we first present the results of 4-MCHO, which has nominal C_s symmetry, followed by the 3- and 2- MCHO radicals.

6.3.1 4-MCHO

DF spectra of 4-MCHO (Figure 6.2) were recorded by pumping six vibronic bands of its LIF spectrum, namely, bands A-F. With the origin band (band A at 26906 cm⁻¹) pumped, there is a peak in the DF spectrum at 76 cm⁻¹ red-shifted from the excitation wavenumber.

The intensity of this peak is slightly stronger than the fluorescence emission to the vibrational ground level of the $\tilde{X}$ -state, i.e., the zero-red-shift $\tilde{B}^2A' \rightarrow \tilde{X}^2A''$ origin band in the DF spectrum. DFT calculations predict $\tilde{X}$ -state vibrational modes with frequencies as low as 109 cm^{-1} . However, the FCF of transition from the vibrational ground level of the $\tilde{B}$ -state to this vibrational level is negligible. DFT calculations predict an $\tilde{A}$ - $\tilde{X}$ separation of 168 cm^{-1} (without ZPE corrections). The DF peak at 76 cm^{-1} is therefore assigned to the origin band of the $\tilde{B}^2A' \rightarrow \tilde{A}^2A'$ transition.

When bands C and E were pumped, low-frequency peaks were observed at 77 and 74 cm^{-1} , respectively. They are assigned to transitions from the corresponding vibrational levels of the $\tilde{B}^2A'$ state to the ground vibrational level of the $\tilde{A}^2A'$ state. The $\tilde{A}$ - $\tilde{X}$ separation of 4-MCHO is therefore determined to be $76(5)\text{ cm}^{-1}$, taken as the averaged value of the low-frequency peaks. Intensities of these peaks with bands A, C, and E pumped are close to the zero-red-shift DF origin bands. Noticeably, with bands B, D, and F pumped, the fluorescence emission to the vibrational ground level of the $\tilde{A}$ -state is extremely weak (pumping band B) or absent (pumping bands D and F). In section 6.2 we will argue that relative intensities of the $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ bands are determined by the vibronic symmetry of the pumped LIF bands: The differences in relative intensities of the DF origin bands are due to the fact that bands A, C, and E are transitions to a' (symmetric) vibrational levels of the $\tilde{B}$ state, whereas bands B, D, and F are to a'' (antisymmetric) levels.³⁶ Note that transitions to the a'' levels are allowed due to the pJT interaction between the $\tilde{A}$ and $\tilde{X}$ states.

Besides the two origin bands, the DF spectrum by pumping band A is dominated by a progression of strong peaks. The most prominent peaks of each member of the

progression are found at 1121, 2165, and 3197 cm^{-1} . These three peaks and the $\tilde{B} \rightarrow \tilde{A}$ origin band at 76 cm^{-1} form a vibrational progression. They are hence assigned to transitions to vibrational levels of the $\tilde{A}$ state. Because of the large difference between the $\tilde{B}$ -state and $\tilde{A} / \tilde{X}$ -state CO bond lengths, one expects transitions to those lower-state vibrational modes that contain significant CO stretch character to have large FCFs and hence stronger intensities. Indeed, DFT calculations predict an $\tilde{A}$ -state CO stretch mode with a vibrational frequency of 1060 cm^{-1} , close to the experimentally observed fundamental frequency of 1045 cm^{-1} , taken as the interval between the strongest peak of the second member of the progression and the $\tilde{A} \rightarrow \tilde{X}$ origin band. The strong progression is, therefore, assigned to $\tilde{A}$ -state CO stretch levels (Figure 6.2). FCF calculations predict strong transitions to the $\tilde{A}$ -state CO stretch levels (Figure 6.3). On the contrary, transitions to the $\tilde{X}$ -state CO stretch levels are significantly weaker. The reason for weaker transitions to the vibrational levels of the $\tilde{X}$ state is discussed in section 6.4.2.

Second member of the CO stretch progress has three distinctive peaks: $\tilde{\nu}_x = 1006$ cm^{-1} , $\tilde{\nu}_y = 1121$ cm^{-1} , and $\tilde{\nu}_z = 1170$ cm^{-1} (Figure 6.2). Peaks at $\tilde{\nu}_x$ and $\tilde{\nu}_z$ are attributed to transitions to other vibrational levels with CO stretch character or combination levels of CO stretch mode with low-frequency modes (Figure 6.3). However, definitive assignments are avoided due to the congestion of transitions. In the region of larger redshift (>1500 cm^{-1}), the third and fourth members of the CO stretch progression are observable. Six peaks are partially resolved in the region of the first overtone of the CO stretch (i.e., the third member of the progression, Figure 6.2). They are attributed to the overtone and combination bands of ν_x , ν_y , and ν_z . The peaks in the region of $3 \nu_{\text{CO}} (\tilde{A})$ (the fourth member

of the CO stretch progression) are unresolved due to the increased density of vibrational levels.

The experimentally observed DF spectrum pumping the LIF origin band is compared with the calculated transition intensities and simulated spectra in Figure 6.3. In the simulation, the $\tilde{B} \rightarrow \tilde{A}$ origin band is shifted to the red with respect to the $\tilde{B} \rightarrow \tilde{X}$ origin band by the experimentally determined $\tilde{A}-\tilde{X}$ separation. The intensities of the $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ transitions are scaled so that the relative intensities of the origin bands match the experimentally obtained spectrum. The simulation semiquantitatively reproduces the spectrum in terms of both transition frequencies and intensities. The calculations correctly predict that the $\tilde{B} \rightarrow \tilde{A}$ transitions to vibrationally excited levels are significantly stronger than the $\tilde{B} \rightarrow \tilde{X}$ transitions. However, although the FCF calculation predicts several weak transitions other than origin bands and the CO-stretch progression, these transitions were not observed in the DF spectrum.

When LIF bands other than A were pumped, the emission to the CO stretch levels (bands x, y, z, as well as their overtone and combination bands) is much weaker except in the case of pumping band E. Band E was assigned to the transition to the ν_{27} level of the $\tilde{B}$ state,³⁶ which has significant CO stretch character. The presence of the transitions to the CO stretch levels of the $\tilde{A}$ -state with band E pumped can, therefore, be again explained by large FCFs. On the contrary, significantly smaller FCFs between other pumped vibrational modes (for bands B, C, D, F) and the CO stretch mode are expected.

With bands B–F pumped, DF bands other than the origin bands appear in the low-frequency region ($<1000\text{ cm}^{-1}$) as labeled by lowercase letters b–f in Figure 6.2. The redshifts of these peaks relative to the $\tilde{B} \rightarrow \tilde{A}$ origin band are close to (but not exactly equal to) the LIF pumping frequencies relative to the $\tilde{B} \leftarrow \tilde{X}$ origin band (Table 6.1). This is due to the large vibrational wave function overlap between the $\tilde{A}$ and $\tilde{B}$ -state levels of the same, non-CO-stretch mode because the only significant geometry change upon excitation is the elongation of the CO bond and mixing between non-CO-stretch vibrational modes is expected to be small. The difference between the redshift of the DF band (with respect to the $\tilde{B} \rightarrow \tilde{A}$ origin) and the relative frequency of the pumped LIF band (relative to the $\tilde{B} \leftarrow \tilde{X}$ origin, i.e., band A) is therefore attributed to the small difference between the $\tilde{A}$ - and $\tilde{X}$ -state vibrational frequencies of the same mode. DF transitions to the $\tilde{X}$ -state levels of these modes were also observed, although the intensities are much lower. The disparity between the $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ transition intensities will be discussed in section 6.4.2. $\tilde{A}$ – $\tilde{X}$ separation of these vibrational levels are close to that of the vibrational ground level, except for that of band e, which is 100 cm^{-1} (Table 6.1).

In the DF spectrum with band F pumped, the peak at 339 cm^{-1} coincides in redshift with band b in the DF spectrum pumping band B. It is hence labeled b' in Figure 6.2. Such an observation confirms the previous assignment of band F to a combination band of the vibrational mode of band B (ν_{55}) and another vibrational mode (ν_{30}).³⁶ Band b' is therefore assigned to the transition to ν_{55} vibrational level of the $\tilde{A}$ state, whereas the other DF peak in the low-frequency region (band f) to the $\nu_{55} + \nu_{30}$ level of the $\tilde{A}$ state.

The most noticeable difference between DF spectra obtained by pumping the LIF origin band (band A) and other vibronic bands is that the prominent vibrational progression observed in the former case is shifted to the red in the latter case. The amount of such a redshift is equal to the redshift of the FC favored transition (bands b–f) with respect to the $\tilde{B} \rightarrow \tilde{A}$ origin band, i.e., the $\tilde{A}$ -state vibrational frequency of the pumped mode. For instance, in the DF spectrum with band E pumped, the frequency interval between the $\tilde{B} \rightarrow \tilde{A}$ origin band (74 cm^{-1}) and band e (648 cm^{-1}) matches that between the $\tilde{A}$ state CO stretch band (1124 cm^{-1}) and the strong peak at 1705 cm^{-1} within the error bars (Table 6.1). Therefore, if the DF spectra are shifted to the blue by the observed $\tilde{A}$ -state frequencies of the pumped modes so that bands b–f are aligned with the $\tilde{B} \rightarrow \tilde{A}$ origin band, all DF spectra of 4-MCHO will have the same vibrational progressions (Figure 6.7). Such an observation implies that when a vibronic level other than the CO stretch levels is pumped, the transition with the largest FCF is not to the $\tilde{A}$ -state CO stretch level or the vibrational level of the pumped mode, but to the combination level of the CO stretch mode and the pumped mode. Figure 6.7 also confirms that all strong peaks observed in the DF spectra except the zero-red-shift bands should be assigned to transitions to the $\tilde{A}$ -state levels rather than the $\tilde{X}$ -state levels.

Redshifts of DF bands of 4-MCHO are summarized in Table 6.1 with their assignments. To elucidate the vibrational assignments, the relative wavenumbers with respect to the $\tilde{B} \rightarrow \tilde{A}$ origin or $\tilde{A}$ -state vibrational levels (bands b–f) are also listed.

6.3.2 3-MCHO

DF spectra of the 3-MCHO isomer (Figure 6.4) were recorded by pumping six LIF bands: the origin band A, fundamental bands B and C, CO-stretch band A*, and bands B* and C*, which are combination bands of vibrational modes of bands B and C with the CO stretch mode. The averaged $\tilde{A}$ - $\tilde{X}$ separation by pumping the LIF bands is 62(5) cm⁻¹. The relative intensities of the $\tilde{B} \rightarrow \tilde{A}$ and $\tilde{B} \rightarrow \tilde{X}$ origin bands are different with different LIF bands pumped. With band A (the LIF origin band) pumped, the origin band of the $\tilde{B} \rightarrow \tilde{A}$ transition in the DF spectrum is stronger than that of the $\tilde{B} \rightarrow \tilde{X}$ transition. Similar relative intensities were observed in the DF spectrum of 4-MCHO when the LIF origin band was pumped (Figure 6.2), suggesting similar electron configurations for the $\tilde{A} / \tilde{X}$ state of these two isomers. This has been predicted by DFT calculations (Figure 6.1). With bands B and C pumped, the relative intensities of the two origin bands in the DF spectra are reversed: the $\tilde{B} \rightarrow \tilde{A}$ origin band is significantly weaker than the $\tilde{B} \rightarrow \tilde{X}$ one. This is similar to the DF spectra of 4-MCHO with a'' levels of the $\tilde{B}$ state pumped, in which the $\tilde{B} \rightarrow \tilde{A}$ transitions are extremely weak or absent. Such reversion, therefore, suggests that vibrational modes of bands B and C of 3-MCHO would be antisymmetric (a'') if the methyl group was replaced by a hydrogen atom.

When band A is pumped, a strong progression is observable and assigned to transitions to CO stretch levels. The most prominent peaks in the members of the progression are at 1105, 2113, and 3120 cm⁻¹. They are transitions to the $\tilde{A}$ state CO stretch levels based on the energy intervals. The peak at 1028 cm⁻¹ is assigned tentatively to the $\tilde{X}$ -state CO stretch level. The $\tilde{A}$ - $\tilde{X}$ separation of the CO stretch level so determined is larger

than that of the vibrational ground levels (77 cm^{-1} vs. 62 cm^{-1}), a phenomenon that was also observed in the DF spectrum of tert-butoxy.¹⁴² Simulation using Gaussian09 and ezSpectrum (Figure 6.3) correctly predicts strong transitions in the CO stretch region. However, the predicted frequency of the CO stretch mode is not as accurate as for the 4-MCHO isomer. In addition, they predict overtone transitions weaker than the fundamental, whereas, in the experimentally obtained spectrum, the overtone bands are stronger.

A doublet (b or c) was observed in the DF spectra when either band B or C was pumped, corresponding to the transition to the vibrational levels of the pumped mode in the $\tilde{A}$ and $\tilde{X}$ states (bands b and c in Figure 6.4). Unlike in the case of 4-MCHO, for which transitions to the $\tilde{X}^2A''$ state vibrational levels are completely absent or much weaker than to the $\tilde{A}^2A'$ state, the two peaks of the doublets in the 3-MCHO DF spectra are of comparable intensities, although the $\tilde{B} \rightarrow \tilde{A}$ transitions are still stronger than the $\tilde{B} \rightarrow \tilde{X}$ ones. This is due to the lowered symmetry and hence, less strict selection rules (section 6.2). Similar to 4-MCHO, with bands B and C pumped, the DF spectra of 3-MCHO are dominated by progressions of combination bands of CO stretch and the pumped modes.

When band A* (CO-stretch band) was pumped, a strong CO stretch progression was observed. The DF spectrum by pumping band B* (combination band) is dominated by a progression of combination bands of CO stretch and the pumped mode. In both cases, the fourth member of the progressions was obscured by the unstructured DF signal, most probably due to excited-state intramolecular vibrational energy redistribution (IVR).³⁴ The first member of the progression in the DF spectrum pumping band B* is labeled b' in Figure

6.4. Such progression becomes very weak when band C* is pumped. Its first member is labeled c' in Figure 6.4.

Furthermore, compared to the DF spectra by pumping band A, B, and C, new peaks are observable in those pumping bands A*, B*, and C*. They are asterisked in Figure 6.4. In each spectrum, these new peaks form a second progression that is red-shifted by ~ 680 cm^{-1} from the aforementioned progression of the CO stretch bands or combination bands of the CO stretch. Such a redshift matches the CO stretch frequency of the $\tilde{B}$ state, determined to be 683 cm^{-1} in the LIF spectrum.³⁶ It can, therefore, be explained by excited-state vibrational population relaxation: After LIF band A* (the CO stretch band) is pumped, part of its population relaxes to the vibrational ground state of the $\tilde{B}$ state. Fluorescence from both the CO stretch level and the vibrational ground level are therefore possible. Because fluorescence from both levels was observed with comparable intensities, the vibrational relaxation process and fluorescence process must have comparable time scales, i.e., at the microsecond scale. The mechanism is illustrated in Figure 6.5. When combination bands B* ($\nu_{\text{CO}} + \nu_{54}$) and C* ($\nu_{\text{CO}} + \nu_{51}$) are pumped, the dominant relaxation process is not to the vibrational ground level, but the non-CO-stretch vibrational level (ν_{54} or ν_{51}) (Figure 6.5). In the former case (pumping band B*), the relaxation and fluorescence processes are of comparable rates as fluorescence from both the initial vibrational level ($\nu_{\text{CO}} + \nu_{54}$) upon LIF excitation and from the level after relaxation (ν_{54}) are observed. In the latter case (pumping band C*), the DF signal from the initial vibrational level ($\nu_{\text{CO}} + \nu_{51}$) is very weak, suggesting a rapid relaxation process that outpaces the fluorescence process.

Redshifts and relative wavenumbers of DF bands of 3- MCHO are summarized in Table 6.2 with their assignments. Figure 6.8 illustrates the DF spectra of 3-MCHO when they are blue-shifted by the $\tilde{A}$ state frequency of the pumped non-CO-stretch modes. The progressions are aligned in the shifted spectra.

6.3.3 2-MCHO

DF spectra of the 2-MCHO isomer (Figure 6.6) were recorded by pumping six LIF bands, labeled A–F in ref.³⁶ The $\tilde{A}$ – $\tilde{X}$ separation of 2-MCHO is 110(5) cm^{-1} , determined as the energy separation between the first two strong peaks in the DF spectra. Similar to 3- and 4-MCHOs, the relative intensities of these two peaks vary depending on the LIF peaks pumped. Transitions to $\tilde{A}$ - and $\tilde{X}$ -state levels of the pumped vibrational modes were also observed (bands b–f in Figure 6.6). Also observed are the $\tilde{A}$ -state CO stretch progression (when band A was pumped) or progressions of combination bands of CO stretch and the pumped modes (when bands B–F were pumped). FCFs calculations qualitatively reproduce the experimental spectrum (Figure 6.3). Figure 6.9 illustrates the coincidence of progressions in the DF spectra after the blue shift. Table 6.3 summarizes redshifts, relative wavenumbers, and assignments.

In the case of pumping band F, a peak at 232 cm^{-1} red shift was observed in the DF spectrum. DFT calculation does predict an $\tilde{X}$ state methyl torsion mode of 229 cm^{-1} for 2-MCHO. Band F was previously assigned to ν_{47} , the ring breathing mode. It is unlikely that these two modes are connected by considerable off-diagonal FCF. Band F in the LIF

spectrum should, therefore, probably be reassigned to the combination band of methyl torsion (calculated to be 230 cm^{-1}) and ν_{54} (calculated to be 288 cm^{-1} and illustrated in Figure 6.10).

6.4 Discussion

6.4.1 Conformational and Vibrational Assignments

In ref.³⁶, LIF bands of 2-, 3-, and 4-MCHOs were assigned to the lowest-energy conformer of each isomer with diequatorial structure. In the present work, the single-conformer assignments have been confirmed by the experimentally obtained DF spectra on the basis of the similarity between DF spectra pumping different LIF bands of each isomer.

In the cases of all three isomers, DF spectra are dominated by a CO stretch progression when the origin band or the CO stretch band in the LIF spectrum (e.g., bands A and A* of 3- MCHO) is pumped. This has been observed in DF spectra of all primary and secondary chain alkoxy radicals,³⁴ as well as cyclohexoxy,³⁵ which was attributed to the large FCFs for such transitions because of the large difference in $\tilde{X}/\tilde{A}$ - and $\tilde{B}$ -state CO bond lengths ($\Delta R_{\text{CO}} \sim 0.2\text{ \AA}$). When other vibronic bands in the LIF spectra were pumped, DF transitions to the ground state vibrational level of the same vibrational mode as the pumped band were observed because of large FCFs of such transitions. Also observed were combination bands of the pumped mode with the CO stretch modes. The combination bands have even higher intensities than the fundamental band of the pumped mode. Such a phenomenon was previously observed in the DF spectra of cyclohexoxy³⁴ and can also

be explained on the basis of the evaluation of FCFs: The large difference between CO bond lengths of the $\tilde{X}/\tilde{A}$ - and the $\tilde{B}$ -states causes rotation of vibrational normal coordinates upon electronic excitation. The ground-state normal coordinates of vibrational modes (other than CO stretch) are mixed with those of the CO stretch modes in the excited state (Duschinsky mixing), and they are coupled in the vibrational overlap integrals. As a result, when non-CO-stretch vibrational levels of the $\tilde{B}$ state are pumped, the DF transitions with the largest FCFs are those to the combination levels of the pumped mode and CO stretch. Similar combination bands were observed in other molecules with large geometry change upon excitation, for instance, in the photoelectron spectra of the $\tilde{B}^2B_2$ state of H_2O^+ : Because of the large change in the $\angle HOH$ angle between the neutral molecule and the cation (104° vs 57°), pure excitation of the ν_1 vibrational mode (symmetric stretch) is not observed. Instead, the photoelectron spectra are dominated by combination bands of ν_1 and ν_2 (bending mode).^{143, 144} Another example that, like MCHOs, also involves vibronic interactions is the Herzberg–Teller (HT)-allowed $\tilde{A}^1B_{2u} \leftarrow \tilde{X}^1A_{1g}$ transition of benzene, in which the HT mode ν_6 (e_{2g}) reveals itself in combination with the totally symmetric ν_1 (a_{1g}) because of the large difference in C–C bond length between the $\tilde{X}$ and the $\tilde{A}$ state ($\Delta r_{CC} = 0.0353$ Å).¹⁴⁵

It is worth noting that the Duschinsky mixing is closely related to vibronic interactions. It has been argued theoretically that vibronic interaction, such as the HT effect, introduces the Duschinsky rotation and breaks the mirror symmetry between the fluorescence and the absorption spectra because of the effect of Duschinsky mixing on transition intensities should be more pronounced for transitions to vibronically coupled

states than those from them.¹⁴⁶ Because of the similarity between the HT effect and the pJT effect, such a difference is expected for pJT molecules such as MCHOs too. Moreover, theory also shows that spectroscopic manifestations of the Duschinsky mixing are likely to be more pronounced in molecules with lower symmetry and larger size,¹⁴⁷ which may explain the observation of the “shift effect” (Figures 6.7-9) in the DF spectra of MCHOs and cyclohexoxy but not the methoxy radical and straight-chain alkoxy radicals. Although a theoretical analysis of the connection between the pJT effect and the Duschinsky mixing is out of the scope of the present work, the experimentally observed DF spectra suggest a close relation between these two effects.

6.4.2 Symmetry of $\tilde{A} / \tilde{X}$ States and Transition Intensities

Previously, the symmetries of the $\tilde{A} / \tilde{X}$ state of primary and secondary chain alkoxyes with C_s geometry as well as cyclohexoxy were determined experimentally on the basis of the analysis of the rotational structure. It has been concluded that the $\tilde{X}$ state of ethoxy,²⁴ all-trans conformers of 1-propoxy, as well as other larger primary alkoxyes,^{88, 134, 138} and cyclohexoxy³³ are of A'' symmetry, whereas that of isopropoxy is an A' state.¹³² The differences were explained by the interaction between the p_x (in the C_s plane) and p_y (perpendicular to the C_s plane) orbitals of the oxygen atom and the alkyl group, which stabilizes the free radical. The overlap of a fully occupied p-orbital with the methyl group has a more significant stabilization effect than a half-filled one. In the case of primary alkoxy radicals and the cyclohexoxy radicals, the p_x orbital is extended toward the alkyl

groups. The electron configuration with fully occupied p_x orbital and half-filled p_y orbital, therefore, has lower energy so that the ground electronic state has A'' symmetry. For isopropoxy, the p_y orbital has a better overlap with the two methyl groups, and hence the electronic state with A' symmetry has lower energy. Interaction between the O atom and the methyl groups in 4-MCHO is similar to that of cyclohexoxy; a $\tilde{X}^2A''$ state is therefore expected, which is consistent with quantum chemical calculations.

No rotationally resolved spectra of 4-MCHO have been obtained. Therefore, definitive experimental evidence of its $\tilde{X} / \tilde{A}$ state symmetry is still elusive. However, relative intensities of the $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ origin bands in the DF spectra (Figure 6.2) support the conjecture above that the ground electronic state of 4-MCHO has A'' symmetry. Theoretical analysis of the electric transition dipole moment (TDM) for the $\tilde{B}-\tilde{X}$ and $\tilde{B}-\tilde{A}$ transitions was provided in refs.^{33, 132} The $\tilde{B}^2A'-\tilde{X} / \tilde{A}^2A'$ TDM is dominated by the HT type effect because of the difference between the permanent dipole moment (PDM) of the upper and lower states. Because the difference in PDM is mainly due to the large variation of the CO bond length upon excitation, the HT-induced TDM is oriented approximately along with the CO bond, defined to be the z-axis. Based on symmetry argument, the TDM of the $\tilde{B}^2A'-\tilde{X} / \tilde{A}^2A''$ transition is along the y-axis, defined as perpendicular to the Cs plane, and has the same magnitude as the x-component of the TDM of the $\tilde{B}^2A'-\tilde{X} / \tilde{A}^2A'$ transition, which is much smaller than its z component. The $\tilde{B}^2A'-\tilde{X} / \tilde{A}A''$ TDM is therefore expected to be significantly smaller than that of the $\tilde{B}^2A'-\tilde{X} / \tilde{A}A'$ transition if no coupling between the $\tilde{A}$ and $\tilde{X}$ states is involved. Although coupling between these two states via SO interaction reduces the difference between the intensities of the $\tilde{B}^2A'-\tilde{X} / \tilde{A}$

$^2A'$ and $\tilde{B} \rightarrow \tilde{A}' - \tilde{X} / \tilde{A} \rightarrow \tilde{A}''$ transitions,¹²² the former is still of stronger intensity than the latter. In addition, the zero-red-shift peaks may contain scattering of the LIF excitation laser, although the gate delay time in the DF experiment was significantly long compared to the laser pulse duration. The relatively stronger $\tilde{B}-\tilde{A}$ origin band in the DF spectrum of 4-MCHO with the LIF origin band pumped, therefore, supports the prediction of quantum chemical calculations that its ground electronic state has A'' symmetry.

When symmetric vibrational modes of the $\tilde{B}$ state of 4-MCHO are pumped, using a similar symmetry argument, the $\tilde{B} \rightarrow \tilde{A}$ origin band in the DF spectra is expected to be stronger than the $\tilde{B} \rightarrow \tilde{X}$ one the same as when the LIF origin band is pumped. On the contrary, when antisymmetric vibrational modes are pumped, the relative intensities are reversed: the $\tilde{B}-\tilde{X}$ band has a higher intensity. The intensity pattern can, therefore, be used to determine the vibrational symmetry of the upper level of the LIF transition. Such a conclusion is consistent with all vibronic assignment in ref.³⁶ except for band D of 4-MCHO at 441 cm^{-1} relative to the LIF origin band), which was assigned to $\nu_{28}(a')$. We reassign band D to $\nu_{53}(a'')$, predicted to be at 463 cm^{-1} by CASSCF calculations.³⁶

The 2- and 3-MCHO radicals do not have C_s symmetry. However, the calculations also predict that, like 4-MCHO, their $\tilde{X}$ states have the half-filled p_x orbital oriented perpendicular to the C_s plane, i.e., a “pseudo- A'' state” with half-filled p_y orbitals. Such a prediction has been confirmed by the DF spectra of these two isomers with the LIF origin band pumped, in which the $\tilde{B}-\tilde{A}$ origin bands have higher intensity.

In the DF spectra of all three isomers, fluorescence emissions to vibrationally excited levels are dominated by transitions to the $\tilde{A}$ rather than the $\tilde{X}$ state levels. In the case of 4-MCHO, the latter transitions are often unobservable, probably because of the high symmetry of 4-MCHO compared to the other two isomers. As discussed above, the A'' state steals intensity from the A' state through SO interaction. The observed difference in transition intensities between DF transitions to the vibrational ground levels and vibrationally excited levels of the $\tilde{A} / \tilde{X}$ state may suggest smaller SO interaction between the vibrationally excited levels of the $\tilde{A}$ and $\tilde{X}$ states than their vibrational ground levels.

6.4.3 $\tilde{A}$ – $\tilde{X}$ Separation

The experimentally determined energy separation between the $\tilde{A}$ and $\tilde{X}$ states and their symmetries can be used to test ab initio calculations. In the previous works on ethoxy,²⁴ isopropoxy¹³² and cyclohexoxy,³³ DFT calculations correctly predicted the energy ordering of the A' and A'' states and semiquantitatively the magnitude of the $\tilde{A}$ – $\tilde{X}$ separation. In the present work on 4-MCHO the DFT calculations demonstrate the same level of accuracy. For isomers without C_s symmetry, 2-MCHO and 3-MCHO, such strategy does not work. Prediction of $\tilde{A}$ – $\tilde{X}$ separations using other quantum chemical methods such as CASSCF are in process.

Within the three isomers studied in the present work, 2-MCHO shows a uniquely large $\tilde{A}$ – $\tilde{X}$ separation as well as smaller $\tilde{B}$ – $\tilde{X}$ excitation energy.³⁶ Both observations may be explained by the interaction between the oxygen atom and the methyl group: Of the three

isomers, the methyl group is closest to the oxygen atom in 2-MCHO and hence the strongest interaction.

6.5 Conclusions

DF spectra of 2-, 3-, and 4-MCHO radicals have been observed under jet-expansion conditions. Some important information about MCHO radicals has been obtained in analyzing the DF spectra, including (i) the energy separations between ground vibrational levels of the ground electronic state ($\tilde{X}$) and the low-lying electronic state ($\tilde{A}$), (ii) the vibrational structure of these two states, and (iii) relative intensities of transitions from the vibronic levels of the high-lying $\tilde{B}$ state to the vibrational levels of the lower states. The DF spectra are dominated by the CO stretch progression when the origin band or the CO stretch band of the LIF spectra is pumped. When other vibronic bands are pumped, progressions of the CO stretch modes combined with the pumped mode are observed. The experimentally obtained spectra provide benchmarks to quantum chemical calculations in terms of energies of electronic states, vibrational frequencies in pJT-coupled states, and FCFs of vibronic transitions to such states. Evidence for vibrational population relaxation in the $\tilde{B}$ state following photoexcitation has been observed. Such relaxation is from the CO stretch level to the ground vibrational level or from combination levels of CO stretch and other vibrational modes to those of the non-CO stretch modes.

Table 6.1. Red Shifts (“rs”) from the Pumped LIF Bands (A–F) and Relative Wavenumbers (“rel”) Observed in the DF Spectra of 4-MCHO (cm⁻¹)^a.

A ($T_{00}^{\tilde{B} \leftarrow \tilde{X}}$)			B (+268)			C (+358)			D (+437)			E (+538)			F (+626)			assignment
rs	rel		rs	rel		rs	rel		rs	rel		rs	rel		rs	rel		
0			0			0			0			0			0			$T_{00}^{\tilde{B} \leftarrow \tilde{X}}$
76						77						74						$T_{00}^{\tilde{B} \rightarrow \tilde{A}}$
			256		w	358		w	435		w	548		w	337	261 ^b	[b’]	$\tilde{A}_{\text{pump}}$
			336	260 ^b	[b]	437	361 ^b	[c]	518	442 ^b	[d]	648	572 ^b	[e]	631		w	$\tilde{X}_{\text{pump}}$
1006	930 ^b	[x]	1025	949 ^b	w	1007	931 ^b	w	1010	934 ^b	w	1009	933 ^b		708	632 ^b	[f]	$\tilde{A}_{\text{pump}}$
1121	1045 ^b	[y]	1098	1022 ^b	w	1126	1050 ^b	w	1079	1003 ^b	w	1124	1048 ^b					$\tilde{A}_{\text{pump}}$
1170	1094 ^b	[z]	1173	1097 ^b	w	1174	1098 ^b	w	1159	1083 ^b	w	1169	1093 ^b					$\tilde{A}_{\text{CO}}$
															1268	931 ^c		$\tilde{A}_{\text{CO}} + \tilde{A}_{\text{pump}}$
															1387	1050 ^c		
															1445	1108 ^c		
			1267	931 ^c		1374	937 ^c		1440	922 ^c		1577	929 ^c		1640	932 ^c		
			1394	1058 ^c		1496	1059 ^c		1560	1042 ^c		1705	1057 ^c		1762	1054 ^c		$\tilde{A}_{\text{CO}} + \tilde{A}_{\text{pump}}$
			1440	1104 ^c		1540	1103 ^c		1608	1090 ^c		1742	1094 ^c		1808	1100 ^c		
1939	1863 ^b	[2x]																$2\tilde{A}_{\text{CO}}$
2055	1979 ^b	[x+y]										2165	2089 ^b					
2111	2035 ^b	[x+z]																
2165	2089 ^b	[2y]																
2208	2132 ^b	[y+z]																
2269	2193 ^b	[2z]																
			2452	2116 ^c		2555	2098 ^c		2606	2088 ^c		2754	2106 ^c		2825	2117 ^c		$2\tilde{A}_{\text{CO}} + \tilde{A}_{\text{pump}}$
3197	3121 ^b																	$3\tilde{A}_{\text{CO}}$

^a Relative wavenumbers are calculated to elucidate vibrational assignments (see footnotes).

Letters in squared brackets correspond to labels in Figure 6.2.

Letter “w” denotes weak DF bands.

^b Redshift relative to the averaged value of $\tilde{A}-\tilde{X}$ separation (76 cm^{-1}). The relative wavenumber corresponds to the $\tilde{A}$ -state vibrational level.

^c Redshift relative to the $\tilde{A}$ -state vibrational frequency of the pumped mode ν_{pump} . The relative wavenumber corresponds to the lower-state CO stretch level. When the combination band F was pumped, two progressions were observed, corresponding to ν_{pump} and $\nu_{\text{pump}'}$. The relative wavenumbers for the former and later progressions are calculated with respect to band f and band b', respectively.

Table 6.2. Red Shifts (“rs”) from the Pumped LIF Bands (A-C, A*-C*) and Relative Wavenumbers (“rel”) Observed in the DF Spectra of 3-MCHO (cm⁻¹)^a.

A (T ₀₀ ^B -X̃)		B (+268)		C (+358)		A* (+437)		B* (+538)		C* (+626)		assignment
rs	rel	rs	rel	rs	rel	rs	rel	rs	rel	rs	rel	
0		0		0		0		0		0		T ₀₀ ^B →X̃
64		64		63		64		61		56		T ₀₀ ^B →Ã
		240		387				238		398		X̃ _{pump}
		312	250 ^b [b]	452	390 ^b [c]			308	246 ^b [b']	458	396 ^b [c']	Ã _{pump}
1028		1025	w	1021	w	684	684 ^d w			1065e	667 ^{c,d}	X̃ _{pump} + v _{CO} ^{B̃}
1105		1098	1036 ^b w	1098	1036 ^b w	752	688 ^d w			1117e	659 ^{c,d}	Ã _{pump} + v _{CO} ^{B̃}
1173	1043 ^b	1160	w	1175	w	1170						X̃ _{CO}
1216		1199	w	1218	w	1221						Ã _{CO}
		1263	1023 ^b	1422	1035 ^c			1260	1022 ^c	1416	1018 ^c	X̃ _{CO} + v _{CO} ^{X̃}
		1352	1040 ^c	1486	1034 ^c			1374	1039 ^c	1508	1050 ^c	Ã _{CO} + v _{CO} ^{Ã}
						1708	684 ^d	1950	690 ^d	2106e	690 ^{c,d}	X̃ _{CO} + v _{CO} ^{X̃}
						1793	688 ^d	2037	690 ^d	2163e	655 ^{c,d}	Ã _{CO} + v _{CO} ^{Ã}
						1856	686 ^d					
						1914	693 ^d					
2113	2051 ^c					2123	2061 ^c					2v _{CO} ^{Ã}
		2365	2053 ^c	2513	2061 ^c			2365	2057 ^c			2v _{CO} ^{Ã} + v _{CO} ^{Ã}
						2811	688 ^d	3050	685 ^d	3165		2v _{CO} ^{Ã} + v _{CO} ^{Ã}
3120	3058 ^b											3v _{CO} ^{Ã} + v _{CO} ^{Ã}

^a Letters in square brackets correspond to labels in Figure 6.4.

^b Redshift relative to the averaged value of the $\tilde{A}-\tilde{X}$ separation (62 cm^{-1}).

^c Redshift relative to the $\tilde{A}$ -state vibrational frequency of the pumped non-CO-stretch mode ν_{pump} .

^d Redshift relative to $n \nu_{\text{CO}} + \nu_{\text{pump}}$. The relative wavenumber corresponds to the $\tilde{B}$ -state CO stretch level.

^e Large uncertainty due to spectral congestion.

Table 6.3. Red Shifts (“rs”) from the Pumped LIF Bands (A–F) and Relative Wavenumbers (“rel”) Observed in the DF Spectra of 2-MCHO (cm⁻¹)^a.

A ($\tau_{00}^{\tilde{B} \rightarrow \tilde{X}}$)		B (+332)		C (+400)		D (+410)		E (+490)		F (+526)		assignment
rs	rel	rs	rel	rs	rel	rs	rel	rs	rel	rs	rel	
0		0		0		0		0		0		$\tau_{00}^{\tilde{B} \rightarrow \tilde{X}}$
111		113		106		111		113		106		$\tau_{00}^{\tilde{B} \rightarrow \tilde{A}}$
										232		
		341		406		423		528		539		$\tilde{\nu}_{\text{pump}}^{\tilde{X}}$
		446	336 ^b [b]	505	395 ^b [c]	524	414 ^b [d]	613	503 ^b [e]	643	533 ^b [f]	$\tilde{\nu}_{\text{pump}}^{\tilde{A}}$
953						952						$\tilde{\nu}_{\text{CO}}^{\tilde{X}}$
1046						1029						
1112	1002 ^b					1120	1009 ^b					$\tilde{\nu}_{\text{CO}}^{\tilde{A}}$
1209						1214						
		1308	967 ^c	1386	980 ^c	1401	978 ^c	1453	925 ^c	1530	991 ^c	$\tilde{\nu}_{\text{CO}}^{\tilde{X}} + \tilde{\nu}_{\text{pump}}^{\tilde{X}}$
		1362		1444		1472		1538		1586		
		1458	1012 ^c	1529	1024 ^c	1542	1018 ^c	1644	1031 ^c	1663	1020 ^c	$\tilde{\nu}_{\text{CO}}^{\tilde{A}} + \tilde{\nu}_{\text{pump}}^{\tilde{A}}$
		1553		1611		1626		1703		1740		
2135	2025 ^b											$2\nu_{\text{CO}}^{\tilde{A}}$
		2512	2066 ^c	2573	2068 ^c	2582	2058 ^c	2702	2089 ^c	2690	2047 ^c	$2\nu_{\text{CO}}^{\tilde{A}} + \tilde{\nu}_{\text{pump}}^{\tilde{A}}$
3134	3024 ^b											$3\nu_{\text{CO}}^{\tilde{A}}$

^a Letters in square brackets correspond to labels in Figure 6.6.

^b Redshift relative to the averaged value of the $\tilde{A}-\tilde{X}$ separation (110 cm^{-1}).

^c Redshift relative to the $\tilde{A}$ -state vibrational frequency of the pumped mode ν_{pump} .

Table 6.4. Calculated vibrational frequencies (cm^{-1}) of $\tilde{X}$ state 4-MCHO (with pseudo-Jahn-Teller distorted geometry) and Franck-Condon factors (FCFs) for transitions from the vibrational ground level of its $\tilde{B}$ state to $\tilde{X}$ state fundamental vibrational levels. (Threshold for FCFs is 0.001.)

assignment	frequency	$ \langle v' v'' \rangle ^2$
ν_0	0	0.0059
ν_{57}	109	
ν_{56}	215	
ν_{55}	234	
ν_{54}	258	
ν_{53}	276	0.0011
ν_{52}	341	
ν_{51}	368	
ν_{50}	417	
ν_{49}	445	
ν_{48}	462	
ν_{47}	584	
ν_{46}	757	0.0013
ν_{45}	792	
ν_{44}	815	0.0015
ν_{43}	880	
ν_{42}	915	0.0016
ν_{41}	938	0.0015
ν_{40}	973	
ν_{39}	984	
ν_{38}	1019	
ν_{37}	1039	0.0020
ν_{36}	1067	0.0012
ν_{35}	1073	0.0019
ν_{34}^a	1122	0.0053
ν_{33}	1140	
ν_{32}	1175	0.0012
ν_{31}	1240	
ν_{30}	1252	
ν_{29}	1271	

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assignment	frequency	$ \langle v' v'' \rangle ^2$
ν_{28}	1294	0.0011
ν_{27}	1333	
ν_{26}	1340	
ν_{25}	1343	
ν_{24}	1351	
ν_{23}	1370	
ν_{22}	1391	
ν_{21}	1410	
ν_{20}	1434	
ν_{19}	1499	
ν_{18}	1506	
ν_{17}	1511	
ν_{16}	1520	
ν_{15}	1521	
ν_{14}	1522	
ν_{13}	2930	
ν_{12}	2992	
ν_{11}	3011	
ν_{10}	3020	
ν_9	3033	
ν_8	3040	
ν_7	3053	
ν_6	3062	
ν_5	3069	
ν_4	3086	
ν_3	3094	
ν_2	3099	
ν_1	3115	

^a CO stretch

Table 6.5. Calculated vibrational frequencies (cm^{-1}) of $\tilde{A}^2A'$ state 4-MCHO and Franck-Condon factors (FCFs) for transitions from the vibrational ground level of its $\tilde{B}^2B'$ state to $\tilde{A}^2A'$ state fundamental vibrational levels. (Threshold for FCFs is 0.001.)

assignment	symmetry	frequency	$ \langle v' v'' \rangle ^2$
ν_0	a'	0	0.0065
ν_{32}	a'	106	
ν_{57}	a''	206	
ν_{56}	a''	232	
ν_{31}	a'	240	0.0014
ν_{55}	a''	256	
ν_{54}	a''	333	
ν_{30}	a'	372	
ν_{29}	a'	415	0.0015
ν_{53}	a''	440	
ν_{28}	a'	458	0.0030
ν_{27}	a'	590	
ν_{26}	a'	763	
ν_{52}	a''	782	
ν_{51}	a''	809	
ν_{25}	a'	823	
ν_{50}	a''	899	
ν_{24}	a'	951	0.0023
ν_{49}	a''	966	
ν_{23}	a'	969	0.0011
ν_{22}	a'	1023	
ν_{48}	a''	1038	
ν_{21}^a	a'	1060	0.0122
ν_{47}	a''	1079	
ν_{20}	a'	1087	
ν_{46}	a''	1135	
ν_{19}	a'	1171	0.0030
ν_{45}	a''	1204	
ν_{18}	a'	1220	0.0018
ν_{44}	a''	1248	

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assignment	symmetry	frequency	$ \langle v' v''\rangle ^2$
v ₁₇	a'	1279	0.0013
v ₁₆	a'	1297	
v ₁₅	a'	1342	
v ₄₃	a''	1342	
v ₄₂	a''	1347	
v ₁₄	a'	1377	
v ₄₁	a''	1388	
v ₁₃	a'	1408	
v ₁₂	a'	1430	
v ₄₀	a''	1499	
v ₃₉	a''	1503	
v ₁₁	a'	1511	
v ₁₀	a'	1519	
v ₃₈	a''	1521	
v ₉	a'	1522	
v ₈	a'	2837	
v ₇	a'	2989	
v ₃₇	a''	3003	
v ₆	a'	3011	
v ₅	a'	3032	
v ₃₆	a''	3033	
v ₄	a'	3038	
v ₃₅	a''	3059	
v ₃	a'	3063	
v ₃₄	a''	3089	
v ₂	a'	3091	
v ₁	a'	3093	
v ₃₃	a''	3099	

^a CO stretch

Table 6.6. Calculated vibrational frequencies (in cm^{-1}) of $\tilde{X}$ state 3-MCHO and Franck-Condon factors (FCFs) for transitions from the vibrational ground level of its $\tilde{B}$ state to $\tilde{X}$ state fundamental vibrational levels. (Threshold for FCFs is 0.001.)

assignment	frequency	$ \langle v' v'' \rangle ^2$
v_0	0	0.0051
v_{57}	146	
v_{56}	162	
v_{55}	232	
v_{54}	256	0.0010
v_{53}	287	
v_{52}	358	0.0020
v_{51}	407	
v_{50}	416	
v_{49}	431	
v_{48}	467	
v_{47}	545	
v_{46}	778	
v_{45}	820	0.0018
v_{44}	852	0.0015
v_{43}	873	
v_{42}	886	
v_{41}	938	
v_{40}	962	0.0013
v_{39}	981	
v_{38}	1014	0.0015
v_{37}	1048	0.0015
v_{36}	1076	
v_{35}	1086	
v_{34}^a	1120	0.0038
v_{33}	1143	
v_{32}	1160	
v_{31}	1236	
v_{30}	1264	
v_{29}	1280	

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assignment	frequency	$ \langle v' v'' \rangle ^2$
ν_{28}	1295	
ν_{27}	1306	
ν_{26}	1342	
ν_{25}	1348	
ν_{24}	1370	
ν_{23}	1380	
ν_{22}	1387	
ν_{21}	1401	
ν_{20}	1430	
ν_{19}	1502	
ν_{18}	1505	
ν_{17}	1512	
ν_{16}	1519	
ν_{15}	1521	
ν_{14}	1524	
ν_{13}	2930	
ν_{12}	3002	
ν_{11}	3014	
ν_{10}	3021	
ν_9	3034	
ν_8	3040	
ν_7	3054	
ν_6	3062	
ν_5	3071	
ν_4	3086	
ν_3	3097	
ν_2	3102	
ν_1	3109	

^a CO stretch

Table 6.7. Calculated vibrational frequencies (cm^{-1}) of $\tilde{X}$ state 2-MCHO and Franck-Condon factors (FCFs) for transitions from the vibrational ground level of its $\tilde{B}$ state to $\tilde{X}$ state fundamental vibrational levels. (Threshold for FCFs is 0.001.)

assignment	frequency	$ \langle v' v'' \rangle ^2$
ν_0	0	0.0055
ν_{57}	116	
ν_{56}	182	
ν_{55}	229	
ν_{54}	259	0.0011
ν_{53}	319	
ν_{52}	342	
ν_{51}	348	0.0018
ν_{50}	425	
ν_{49}	431	
ν_{48}	486	
ν_{47}	555	
ν_{46}	760	0.0011
ν_{45}	827	0.0015
ν_{44}	837	
ν_{43}	857	
ν_{42}	900	0.0029
ν_{41}	936	0.0011
ν_{40}	951	0.0019
ν_{39}	991	
ν_{38}	998	
ν_{37}	1064	0.0011
ν_{36}	1080	
ν_{35}	1083	
ν_{34}^a	1123	0.0048
ν_{33}	1138	0.0014
ν_{32}	1171	
ν_{31}	1217	
ν_{30}	1263	
ν_{29}	1268	

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assignment	frequency	$ \langle v' v'' \rangle ^2$
v_{28}	1286	
v_{27}	1325	
v_{26}	1338	
v_{25}	1348	
v_{24}	1374	
v_{23}	1375	
v_{22}	1390	
v_{21}	1396	
v_{20}	1429	
v_{19}	1502	
v_{18}	1507	
v_{17}	1511	
v_{16}	1519	
v_{15}	1522	
v_{14}	1523	
v_{13}	2917	
v_{12}	3007	
v_{11}	3018	
v_{10}	3023	
v_9	3028	
v_8	3034	
v_7	3056	
v_6	3061	
v_5	3068	
v_4	3075	
v_3	3094	
v_2	3114	
v_1	3116	

^a CO stretch

Figure 6.1. Half-filled orbitals of the lowest-energy conformers of (a) 2-MCHO, (b) 3-MCHO, and (c) 4-MCHO. Hydrogen atoms are not shown for clarity except the one at the C_1 -position.

Figure 6.2. DF spectra of 4-MCHO. Numbers in parentheses after the LIF bands are relative wavenumbers with respect to the origin band (band A) at 26906 cm^{-1} .

Figure 6.3. DF spectra of 2-, 3-, and 4-MCHOs by pumping the LIF origin bands compared with calculated transition intensities and simulated spectra. Blue and red sticks represent $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{A}$ transitions, respectively.

Figure 6.4. DF spectra of 3-MCHO. Numbers in parentheses after the LIF bands are relative wavenumbers with respect to the origin band (band A) at 26677 cm⁻¹.

Figure 6.5. Excited-state vibrational population relaxation (wavy arrows) and fluorescence emission (red arrows) after $\tilde{B} \leftarrow \tilde{X}$ excitation (black arrow) of 3-MCHO to CO-stretch combinations bands ($\nu_{\text{CO}} + \nu^*$). $\tilde{X}$ and $\tilde{A}$ states are semi degenerate. Dashed horizontal lines represent vibrational energy levels of the $\tilde{X}$ state.

Figure 6.6. DF spectra of 2-MCHO. Numbers in parentheses after the LIF bands are relative wavenumbers with respect to the origin band (band A) at 26275 cm⁻¹.

Figure 6.7. DF spectra of 4-MCHO. The spectra by pumping vibronic bands other than the origin band (A) in the LIF spectrum are blueshifted by the A-state vibrational frequency of the pumped mode so that the DF bands to the $\tilde{A}$ -state vibrational level of the pumped modes are aligned.

Figure 6.8. DF spectra of 3-MCHO. The spectra by pumping vibronic bands other than the origin band (A) and the CO stretch band (A*) in the LIF spectrum are blueshifted by the A-state vibrational frequency of the pumped mode so that the DF bands to the $\tilde{A}$ -state vibrational level of the pumped modes are aligned.

Figure 6.9. DF spectra of 2-MCHO. The spectra by pumping vibronic bands other than the origin band (A) in the LIF spectrum are blueshifted by the A-state vibrational frequency of the pumped mode so that the DF bands to the $\tilde{A}$ -state vibrational level of the pumped modes are aligned.

Figure 6.10. Figure: B-state vibrational mode ν_{54} of 2-MCHO.

CHAPTER VII

DISPERSED FLUORESCENCE SPECTROSCOPY OF JET-COOLED 1-METHYLCYCLOHEXOXY RADICALS

7.1 Introduction

The cyclohexoxy radical and its methyl substitutions are important reaction intermediates in combustion and atmospheric chemistry.^{148, 149} Spectroscopic investigations can serve as diagnostics of these free radicals in kinetic studies,^{36, 37, 150, 151} and provide information about their structure and dynamics. Previously, laser-induced fluorescence (LIF)³⁷ and dispersed fluorescence (DF)⁹³ spectra of 2-, 3-, and 4-methylcyclohexoxy (MCHO) radicals have been obtained under jet-cooled conditions. Spectral analysis and assignment helped determination of the vibronic structure of these isomers and understanding of the effect of methyl substitution. Furthermore, the LIF spectrum of 1-MCHO was reported by Wu *et al.*³⁷ Significant differences between LIF spectra of the four positional isomers of MCHOs have been found. For instance, strong CO-stretch progressions are present in the LIF spectra of the 4- and 3-MCHO radicals but not in those of 2- and 1-MCHOs. Within all four positional isomers, 1-MCHO is unique due to its tertiary structure and the juxtaposition of the methyl group to the CO bond. In addition, two lowest-energy conformers, chair-axial, and chair-equatorial have been observed in the LIF spectra under

jet-cooled conditions, which further complicates the spectrum. In the present letter, we report the DF spectra of 1-MCHO under jet-cooled conditions. They are significantly different from those of 2-, 3-, and 4-MCHOs, which are similar to one another.

7.2 Quantum Chemical Calculations

1-MCHO radicals, there are two types of conformers, namely, chair conformers and twisted-boat conformers. Calculations predicted the energy barriers from the twisted-boat to the chair conformers are about 3.05–4.96 kcal/mol, while the barriers from chair conformers to twisted-boat conformers are 8.62–10.43 kcal/mol. Thus, twisted-boat conformers are easy to convert to chair conformers.³⁷ The lowest energy conformer of 1-MCHO is a chair-axial conformer in which the oxygen atom is located at the axial orientation, while the methyl group is at the equatorial orientation. On the other hand, chair-equatorial conformer in which oxygen atom is at the equatorial position and the methyl group is at the axial orientation and is 1.60 kcal/mol higher in energy than the chair-axial conformer.³⁷ Both chair-axial and chair-equatorial conformers of 1-MCHO radical have C_s symmetry. Previously, extensive calculations were performed on the $\tilde{X}$ - and $\tilde{B}$ -state 1-MCHO radicals and used to guide the analysis of the experimentally obtained LIF spectra.³⁷ Such analysis allowed the assignment of vibronic bands in the LIF spectra and suggests that all LIF bands observed under jet-cooled conditions are due to the lowest-energy conformers. In the present work, two types of new calculations have been carried out in aid of the analysis of the DF spectra. First, density functional theory (DFT)

calculations at the UCAM-B3LYP/6-311+G(d,p)¹¹² level of theory were performed to predict the energy separation between the $\tilde{X}$ and the $\tilde{A}$ states of two conformers of 1-MCHO, which retains the C_s symmetry of the 1-MCHO radical. This was done by putting the unpaired electron in either p_x or p_y orbitals localized on the oxygen atom. The calculations predict that the ground electronic state ($\tilde{X}$) has A'' symmetry whereas the first excited state ($\tilde{A}$) is of A' symmetry. The energy separation between these two states of chair axial and chair equatorial conformers were found to be 286 cm^{-1} and 206 cm^{-1} (with ZPE corrections). When the molecular symmetry was allowed to be lowered to C_1 for both conformers, geometry optimization resulted in the pJT-distorted structure of the 1-MCHO conformers. The pJT stabilization energy, defined as the energy difference between the ground-state ($\tilde{X}^2A''$) molecule with C_s symmetry and that with C_1 geometry, i.e., no symmetry, was found to be 174 cm^{-1} for chair axial and 151 cm^{-1} for chair equatorial conformer.

Calculated relative energies of 1-MCHO conformers, energy separation between $\tilde{A}$ - and $\tilde{X}$ -states ($\Delta E^{\tilde{A}-\tilde{X}}$) and $\tilde{X}$ - and $\tilde{A}$ -state CO-stretch and C-CH₃-stretch frequencies of 1-MCHO conformers are listed in Table 7.1.

7.3 Results

Selected vibronic bands in the LIF spectrum of 1-MCHO were pumped, and the DF spectra were obtained. The LIF bands are labeled by capital letters following ref.³⁷ DF spectra obtained by pumping eleven bands (B, D, E, F, G, H, I, J, K, L, N) are presented in the

letter . DF spectra pumping most of the other bands are either structureless or of low signal-to-noise ratio, which hinders definitive assignment of the transitions. Band A and Band C in the LIF spectrum are different from other DF spectra obtained. It is therefore attributed to an unknown impurity or some other molecular transitions. DF spectrum pumping band, A and band C, are given in Figure 7.5.

7.3.1 Chair-Axial Conformer

DF spectra obtained by pumping eight vibronic bands (D, F, H, I, J, K, L, N) that belong to the chair-axial conformer are compared in Figure 7.1. In the DF spectrum pumping Band D, the LIF origin band, the first peak other than the zero-redshift one is at 238 cm^{-1} . This peak is hence assigned to the $\tilde{B} \rightarrow \tilde{A}$ origin band, corresponding to an $\tilde{A}-\tilde{X}$ separation of $238(5)\text{ cm}^{-1}$ for the chair-axial conformer. Quantum chemical calculations predicted a large ($\sim 35\text{ m}\text{\AA}$) decrease in C-CH₃ bond length upon $\tilde{B} \leftarrow \tilde{A} / \tilde{X}$ excitation.⁵ Large Franck-Condon factors are therefore expected for transitions from the vibrational ground level of the $\tilde{B}$ state to the C-CH₃ stretch levels of the $\tilde{A} / \tilde{X}$ state. It is also the first member of a vibrational progression with separations of $\sim 486\text{ cm}^{-1}$ (see figure 7.2). It is therefore assigned to the transition to the first C-CH₃ stretch level of the $\tilde{X}$ state. The second member of the aforementioned progression is at 517 cm^{-1} , 755 cm^{-1} above the $\tilde{B} \rightarrow \tilde{A}$ origin band. Hence, this transition is assigned to the C-CH₃ stretch level of the $\tilde{A}$ state. As a comparison density functional theory (DFT) calculations at the UCAM-B3LYP/6-311+G(d) level of

theory predicts fundamental frequencies of 553 cm^{-1} and 569 cm^{-1} for the $\tilde{X}$ -state and $\tilde{A}$ -state C-CH₃ stretch modes, respectively.

The peak at 996 cm^{-1} is assigned to the first overtone of the C-CH₃ stretch of the $\tilde{X}$ -state. The peak at 1267 cm^{-1} is assigned to the first overtone of the C-CH₃ stretch of the $\tilde{A}$ -state. In both $\tilde{X}$ - and $\tilde{A}$ -state transition, we did not observe the CO-stretch transition. Quantum calculation predicted the CO stretch frequencies 925 cm^{-1} and 919 cm^{-1} for $\tilde{X}$ and $\tilde{A}$ -state assigned to the transition to the $\tilde{A}$ -state CO-stretch level. But in the DF spectrum, we did not observe any peak that can be assigned CO-stretch level. The strong peak at 1578 cm^{-1} can be assigned to the combination of CO stretch and C-CH₃ mode.

The strong peaks in the higher-frequency region contain multiple, partially resolved transitions. Transition frequencies were determined in multi-peak fitting to Gaussian shapes. Transition frequencies are summarized in Table 7.2. Three vibrational progressions are determined: $\nu_{\text{C-CH}_3}(\tilde{X})$, $\nu_{\text{C-CH}_3}(\tilde{A})$, and $(n-3)\nu_{\text{C-CH}_3}(\tilde{X}) + \nu_{\text{CO}}(\tilde{X})$ with $n=4-10$ (Figure 7.2). The constant intervals between the progression members suggest the absence of any detectable anharmonicity or Fermi resonance. Although transitions to the fundamental levels of the $\tilde{X}$ - and $\tilde{A}$ -state CO stretch modes were not observed, their vibrational frequencies were determined by vibrational combination differences to be 486 cm^{-1} and 1005 cm^{-1} , respectively.

In the DF spectra of 2-, 3-, and 4-MCHO radicals, transitions to high-energy CO-stretch levels often have broad linewidth and are obscured by background signal due to interaction between highly excited vibrational levels. In the present work of 1-MCHO,

sharp C-CH₃ stretch transitions were observed for $\tilde{X}$ - and $\tilde{A}$ -state. In addition, the intensities of the DF peaks oscillate when the vibrational quantum numbers increase. Explanation of these observations based computational results and theoretical analysis are given in Section 7.4

There is a noticeable difference when the origin (band D) band in the LIF spectrum was pumped, only four strong and resolved peaks (0 cm⁻¹, 1578 cm⁻¹, 3126 cm⁻¹, and 4628 cm⁻¹) were observed in the DF spectrum. These peaks are of equal spacing and are assigned to transitions to the vibrational ground level, the $\nu_{\text{C-CH}_3} + \nu_{\text{CO}}$ level, the $4\nu_{\text{C-CH}_3} + \nu_{\text{CO}}$ level, and the $7\nu_{\text{C-CH}_3} + \nu_{\text{CO}}$ of the $\tilde{X}$ state. A possible mechanism for the difference in transition intensities is discussed in Section 7.4.

When the band N in the LIF spectrum was pumped, the DF structure of the band same as the origin band (band D). Hence band N can be assigned to the transition of CO stretch level of $\tilde{B}$ state.

7.3.2 Chair-Equatorial Conformer

DF spectra of the chair-equatorial conformer (Figure 7.3) were obtained by pumping three vibronic bands: B, E, G. Unlike the chair-axial conformer, the DF spectrum pumping the LIF origin band of the chair-equatorial does not show strong transition and also signal to noise ratio was very bad. In the DF spectrum pumping Band B, the first peak other than the zero-redshift one is at 175 cm⁻¹. This peak is hence assigned to the $\tilde{B} \rightarrow \tilde{A}$ origin band, corresponding to an $\tilde{A}-\tilde{X}$ separation of 175(8) cm⁻¹ for the chair-equatorial conformer.

maybe assigned to the $\tilde{B} \rightarrow \tilde{A}$ origin band. Such an assignment is supported by other experimental evidence (vide infra).

DF spectrum pumping the LIF origin band of the chair-equatorial conformer (Band B) is significantly different from that of the chair-axial conformer. It is also the first member of a vibrational progression with separations of $\sim 703\text{ cm}^{-1}$ (see figure 7.4). It is therefore assigned to the transition to the first C-CH₃ stretch level of the $\tilde{X}$ state. The second member of the aforementioned progression is at 735 cm^{-1} , 910 cm^{-1} above the $\tilde{B} \rightarrow \tilde{A}$ origin band. Hence, this transition is assigned to the C-CH₃ stretch level of the $\tilde{A}$ state. As a comparison density functional theory (DFT) calculations at the UCAM-B3LYP/6-311+G(d) level of theory predicts fundamental frequencies of 708 cm^{-1} and 716 cm^{-1} for the $\tilde{X}$ state and $\tilde{A}$ -state C-CH₃ stretch modes, respectively.

The peak at 1441 cm^{-1} is assigned to the first overtone of the C-CH₃ stretch of the $\tilde{X}$ -state. The peak at 1584 cm^{-1} is assigned to the first overtone of the C-CH₃ stretch of the $\tilde{A}$ -state. In both $\tilde{X}$ - and $\tilde{A}$ -state transition, we did not observe the CO-stretch transition. Quantum calculation predicted the CO stretch frequencies 926 cm^{-1} and 918 cm^{-1} for $\tilde{X}$ and $\tilde{A}$ -state assigned to the transition to the $\tilde{A}$ -state CO-stretch level. However, in the DF spectrum, we did not observe any peak that can be assigned CO-stretch level. The strong peak at 1718 cm^{-1} can be assigned to the combination of CO stretch and C-CH₃ mode.

The strong peaks in the higher-frequency region contain multiple, partially resolved transitions. Transition frequencies were determined in multi-peak fitting to Gaussian shapes. Transition frequencies are summarized in Table 7.3. Three vibrational progressions

are determined: $\nu_{\text{C-CH}_3}(\tilde{X})$, $\nu_{\text{C-CH}_3}(\tilde{A})$, and $(n-2)\nu_{\text{C-CH}_3}(\tilde{X}) + \nu_{\text{CO}}(\tilde{X})$ with $n=3-10$ (Figure 7.4). The constant intervals between the progression members suggest the absence of any detectable anharmonicity or Fermi resonance. Although transitions to the fundamental levels of the $\tilde{X}$ - and $\tilde{A}$ -state CO stretch modes were not observed, their vibrational frequencies were determined by vibrational combination differences to be 703 cm^{-1} and 1015 cm^{-1} , respectively.

In the present work of 1-MCHO, sharp C-CH₃ stretch transitions were observed for $\tilde{X}$ - and $\tilde{A}$ -state. In addition, the intensities of the DF peaks oscillate when the vibrational quantum numbers increase. The explanation of these observations based on computational results and theoretical analysis is given in Section 7.4. There is a noticeable difference when the origin (band B) band in the LIF spectrum was pumped, only four strong and resolved peaks (0 cm^{-1} , 1718 cm^{-1} , 3230 cm^{-1} , and 4715 cm^{-1}) were observed in the DF spectrum. These peaks are of equal spacing and are assigned to transitions to the vibrational ground level, the $\nu_{\text{C-CH}_3} + \nu_{\text{CO}}$ level, the $3\nu_{\text{C-CH}_3} + \nu_{\text{CO}}$ level, and the $5\nu_{\text{C-CH}_3} + \nu_{\text{CO}}$ of the $\tilde{X}$ state.

7.4 Discussion

The $\tilde{A}$ - $\tilde{X}$ separation has been experimentally determined to 238 cm^{-1} for the chair-axial conformer and 175 cm^{-1} for the chair-equatorial conformer. These values shall be compared to DFT-calculated values of 286 cm^{-1} for the chair-axial conformer and 209 cm^{-1} for the chair-equatorial conformer (with zero-point-energy corrections). This is consistent

with the previous conclusion that DFT calculations provide semi-quantitative prediction of the $\tilde{A}-\tilde{X}$ separation of alkoxy radicals.

The vibrational structure of the DF spectra of 1-MCHO is significantly different from those of the other three positional isomers. For 2-, 3-, and 4-MCHOs, DF spectra of emission from the vibrational ground level of the $\tilde{B}$ state are dominated by the CO-stretch progression. On the contrary, DF spectra, by pumping the LIF origin band of the chair-axial conformer of 1-MCHO, has strong progressions that involve both CO stretch and C-CH₃ stretch modes. Such difference is due to different positions of the methyl group on the six-membered ring and the steric interaction between the CO bond and the methyl group of 1-MCHO. For all MCHO isomers, the $\tilde{B} \leftarrow \tilde{X}$ excitation corresponds to the promotion of one electron in the CO bonding orbital to the half-filled orbital on the oxygen atom. It weakens the CO bond and hence increases the bond length. Such increment has been predicted by quantum chemical calculations to be ~ 0.2 Å. Unlike the other three isomers, for 1-MCHO, the oxygen atom and the methyl group are connected to the same carbon atom. The weakening of the CO bond, therefore, allows the strengthening of the C-CH₃ bond due to less steric repulsion. The C-CH₃ bond length of the $\tilde{B}$ -state is 35 mÅ shorter than that of the $\tilde{A} / \tilde{X}$ state according to quantum chemical calculations. Now that both CO and C-CH₃ bond lengths change significantly upon excitation, one expects to observe both CO stretch and C-CH₃ stretch transitions in the DF spectra of 1-MCHO.

The intensity pattern of the progressions of CO stretch and C-CH₃ stretch modes, however, does not follow that of a normal Franck-Condon progression. (See Figure 7.6 and 7.7) Figure 7.2 illustrates the DF spectrum of the chair-axial conformer in the region up to

6500 cm⁻¹ pumping the LIF origin band. The intensities of the DF peaks demonstrate an oscillating pattern with intensity peaks at $\nu_{\text{C-CH}_3}$ ($\tilde{X}$) and $n\nu_{\text{C-CH}_3}$ ($\tilde{A}$) with $n=1,2,4,5$. Such alternation of vibronic band intensity cannot be explained by vibronic interactions such as the pseudo-Jahn-Teller interaction between the $\tilde{A}$ - and $\tilde{X}$ -states or coupling between vibration levels due to Fermi resonance and Coriolis interaction because the frequencies of vibrational levels are unperturbed and progressions with constant spacings have been observed. The most plausible explanation to the oscillating intensity pattern of DF peaks is, therefore, Duschinsky rotation, which affects the intensities of the vibronic bands but not their frequencies. Indeed, in the original paper on the effect later named after him, Duschinsky predicted that two mixed modes would have four combination bands with large transition intensities.¹²² A simulation was attempted but predicted strong CO stretch mode. The CO stretch mode and the C-CH₃ modes are mixed, which hinders quantitative analysis.

The DF spectra of 1-MCHO pumping the LIF origin band of both chair-axial and chair-equatorial are dominated by emission to the $\tilde{X}$ - and $\tilde{A}$ -states. The explanation of this observation is based on the vibronic interaction between the $\tilde{A}$ and $\tilde{X}$ -state and was outlined in our previous work on the other three isomers.⁹³ In brief, for all four isomers, the ground electronic ($\tilde{X}$) state has A'' symmetry, while the first excited ($\tilde{A}$) state is an A' state. The transition dipole moment (TDM) of the $\tilde{B}^0 \text{A}' - \tilde{A}^0 \text{A}'$ transition, lying within the C_s plane, is dominant by the Herzberg-Teller (HT)-induced TDM due to the large difference between the permanent dipole moments (PDMs) of the two states. For the TDM of the $\tilde{B}^0 \text{A}' - \tilde{X}^0 \text{A}''$ transition, which is perpendicular to the C_s plane, its magnitude is expected to be close to

the original (non-HT) TDM component. TDM of the $\tilde{B} A' - \tilde{X} A''$ is therefore significantly weaker than the $\tilde{B} A' - \tilde{A} A'$ transition.

In the DF spectrum of the equatorial conformer pumping the LIF origin band, follow the similar pattern of axial-conformer. Also, DFT calculations, which have correctly predicted the energy ordering of other alkoxy radicals. Another significant difference between the DF spectra of 1-MCHO and other MCHO isomers is that the former has narrow linewidth and partially resolved vibrational structure well into the high energy region, whereas for the latter, the members with large vibrational quantum numbers in the CO progressions are structureless.

DF spectra of the chair-equatorial conformer are lack of the strong progressions observed in that of the chair-axial conformer. This might be partly attributed to the low signal-to-noise ratio. Most probably, however, it is due to the more complicated PES and hence the vibronic structure of the $\tilde{X}/\tilde{A}$ -state PES, a topic that is worth future investigation. Furthermore, emission from the CO-stretch levels of the $\tilde{B}$ state of both conformers shows only transitions to the CO stretch and C-CH₃ stretch combination levels of the $\tilde{X}$ state. No CO stretch transitions to the $\tilde{A}$ -state were observed.

7.5 Conclusions

The $\tilde{A}$ - $\tilde{X}$ separation of the chair-axial and chair-equatorial conformers of the 1-MCHO radical has been experimentally determined to be 238 cm⁻¹ and 175 cm⁻¹, respectively. When the LIF origin band of the chair-axial conformer of 1-MCHO is pumped, its DF

spectrum is dominated by three progressions of C-O stretch and C-CH₃ stretch modes. The intensity pattern of the progressions can be explained by Duschinsky mixing between these two modes.

Table 7.1. Numbers of conformers and their calculated relative energies, energy separation between $\tilde{A}$ -and $\tilde{X}$ -states ($\Delta E^{\tilde{A}-\tilde{X}}$) and $\tilde{X}$ - and $\tilde{A}$ -state CO-stretch and C-CH₃-stretch frequencies of 1-MCHO conformers. $\Delta E^{\tilde{A}-\tilde{X}}$ includes zero-point-energy corrections.

conformer	relative energy (cm ⁻¹)	$\Delta E^{\tilde{A}-\tilde{X}}$	$\nu^{\tilde{X}}_{\text{CO}}$ (cm ⁻¹)	$\nu^{\tilde{A}}_{\text{CO}}$ (cm ⁻¹)	$\nu^{\tilde{X}}_{\text{C-CH}_3}$ (cm ⁻¹)	$\nu^{\tilde{A}}_{\text{C-CH}_3}$ (cm ⁻¹)
axial	0	286	925	919	553	569
equatorial	420	209	926	918	708	716

Table 7.2. Redshifts (r.s.) from the pumped LIF lines and relative wavenumbers (rel.)

observed in the DF spectra of the chair-axial conformer of 1-MCHO (cm^{-1}).

r.s.	cald.	rel. ^a	cald.	assignment
0				$0_0^0 (\tilde{B} \rightarrow \tilde{X})$
238				$0_0^0 (\tilde{B} \rightarrow \tilde{A})$
486	553			$\nu_{\text{C-CH}_3} (\tilde{X})$
755		517	569	$\nu_{\text{C-CH}_3} (\tilde{A})$
996				$2\nu_{\text{C-CH}_3} (\tilde{X})$
1267		1029		$2\nu_{\text{C-CH}_3} (\tilde{A})$
1491				$3\nu_{\text{C-CH}_3} (\tilde{X})$
1578				$\nu_{\text{C-CH}_3} (\tilde{X}) + \nu_{\text{CO}} (\tilde{X})$
1800		1562		$3\nu_{\text{C-CH}_3} (\tilde{A})$
2060				$4\nu_{\text{C-CH}_3} (\tilde{X})$
2315		2077		$4\nu_{\text{C-CH}_3} (\tilde{A})$
2618				$5\nu_{\text{C-CH}_3} (\tilde{X})$
2849		2611		$5\nu_{\text{C-CH}_3} (\tilde{A})$
3055				$6\nu_{\text{C-CH}_3} (\tilde{X})$
3126				$4\nu_{\text{C-CH}_3} (\tilde{X}) + \nu_{\text{CO}} (\tilde{X})$
3341		3103		$6\nu_{\text{C-CH}_3} (\tilde{A})$
3562				$7\nu_{\text{C-CH}_3} (\tilde{X})$
3846		3608		$7\nu_{\text{C-CH}_3} (\tilde{A})$
4072				$8\nu_{\text{C-CH}_3} (\tilde{X})$
4374		4136		$8\nu_{\text{C-CH}_3} (\tilde{A})$
4543				$9\nu_{\text{C-CH}_3} (\tilde{X})$
4628				$7\nu_{\text{C-CH}_3} (\tilde{X}) + \nu_{\text{CO}} (\tilde{X})$
4855		4617		$9\nu_{\text{C-CH}_3} (\tilde{A})$
5057				$10\nu_{\text{C-CH}_3} (\tilde{X})$
5375		5137		$10\nu_{\text{C-CH}_3} (\tilde{A})$
5565				$11\nu_{\text{C-CH}_3} (\tilde{X})$
5876		5638		$11\nu_{\text{C-CH}_3} (\tilde{A})$
6062				$12\nu_{\text{C-CH}_3} (\tilde{X})$
6115				$10\nu_{\text{C-CH}_3} (\tilde{X}) + \nu_{\text{CO}} (\tilde{X})$
6371		6133		$12\nu_{\text{C-CH}_3} (\tilde{A})$

^a Redshift relative to the $\tilde{A}-\tilde{X}$ separation (238 cm^{-1})

Table 7.3. Redshifts (r.s.) from the pumped LIF lines and relative wavenumbers (rel.) observed in the DF spectra of the chair-equatorial conformer of 1-MCHO (cm^{-1}).

r.s.	cald.	rel. ^a	cald.	assignment
0				$0_0^0 (\tilde{B} \rightarrow \tilde{X})$
175				$0_0^0 (\tilde{B} \rightarrow \tilde{A})$
703	708			$\nu_{\text{C-CH}_3} (\tilde{X})$
910		735	716	$\nu_{\text{C-CH}_3} (\tilde{A})$
1441				$2\nu_{\text{C-CH}_3} (\tilde{X})$
1584		1409		$2\nu_{\text{C-CH}_3} (\tilde{A})$
1718				$\nu_{\text{C-CH}_3} (\tilde{X}) + \nu_{\text{CO}} (\tilde{X})$
2219				$3\nu_{\text{C-CH}_3} (\tilde{X})$
2409		2234		$3\nu_{\text{C-CH}_3} (\tilde{A})$
2930				$4\nu_{\text{C-CH}_3} (\tilde{X})$
3126		2951		$4\nu_{\text{C-CH}_3} (\tilde{A})$
3230				$3\nu_{\text{C-CH}_3} (\tilde{X}) + \nu_{\text{CO}} (\tilde{X})$
3644				$5\nu_{\text{C-CH}_3} (\tilde{X})$
3771		3596		$5\nu_{\text{C-CH}_3} (\tilde{A})$
4290				$6\nu_{\text{C-CH}_3} (\tilde{X})$
4487		4312		$6\nu_{\text{C-CH}_3} (\tilde{A})$
4775				$5\nu_{\text{C-CH}_3} (\tilde{X}) + \nu_{\text{CO}} (\tilde{X})$
4902				$7\nu_{\text{C-CH}_3} (\tilde{X})$
5233		5058		$7\nu_{\text{C-CH}_3} (\tilde{A})$
5603				$8\nu_{\text{C-CH}_3} (\tilde{X})$
6220				$7\nu_{\text{C-CH}_3} (\tilde{X}) + \nu_{\text{CO}} (\tilde{X})$

^a Redshift relative to the $\tilde{A}-\tilde{X}$ separation (175 cm^{-1})

Figure 7.1. DF spectra of the chair-axial conformer of 1-MCHO. Numbers in parentheses after the LIF bands are relative wavenumbers with respect to the origin band (Band D) at 27614 cm^{-1} .

Figure 7.2. DF spectrum of band D (27614 cm^{-1}) in the LIF of the chair-axial conformer of 1-MCHO. The asterisks are the assignments of the DF spectrum, $\nu_{\text{C-CH}_3}(\tilde{X})$, $\nu_{\text{C-CH}_3}(\tilde{A})$, and $\nu_{\text{C-CH}_3}(\tilde{X}) + \nu_{\text{CO}}(\tilde{X})$, respectively.

Figure 7.3. DF spectra of the chair-equatorial conformer of 1-MCHO. Numbers in parentheses after the LIF bands are relative wavenumbers with respect to the origin band (Band B) at 27455 cm^{-1} .

Figure 7.4. DF spectrum of band B (27455 cm^{-1}) in the LIF spectrum of the chair-equatorial conformer of 1-MCHO. The asterisks are the assignments of the DF spectrum, $\nu_{\text{C-CH}_3}(\tilde{X})$, $\nu_{\text{C-CH}_3}(\tilde{A})$, and $\nu_{\text{C-CH}_3}(\tilde{X}) + \nu_{\text{CO}}(\tilde{X})$, respectively.

Figure 7.5. DF spectra of unknown LIF bands of 1-MCHO. Numbers in parentheses are the LIF frequencies.

Figure 7.6. Comparison between the experimental (bottom red trace) and simulated (top black trace) DF spectra of the chair-axial conformer of the 1-MCHO radical. The experimental DF spectra were obtained by pumping the origin band in the LIF spectrum (Band D).

Figure 7.7. Comparison between the experimental (bottom red trace) and simulated (top black trace) DF spectra of the chair-equatorial conformer of the 1-MCHO radical. The experimental DF spectra were obtained by pumping the origin band in the LIF spectrum (Band B).

CHAPTER VIII

ROOM-TEMPERATURE CAVITY RING-DOWN SPECTROSCOPY OF METHYLALLYL PEROXY RADICALS

8.1 Introduction

Peroxy radicals are key reaction intermediates formed during the oxidation of hydrocarbons in the atmosphere,^{2, 39} and low-temperature combustion.^{40, 133} Although spectroscopy and kinetics of saturated straight-chain peroxy radicals have been extensively investigated, and fewer studies have been done on unsaturated peroxy radicals.^{72, 152-154} In particular, many intermediates in the oxidation of conjugated olefins contain the allyl peroxy radical functionality.^{68, 71} This functionality is also present in four of the six possible isomers of peroxy radicals formed in OH-initiated oxidation of 2-methyl-1,3-butadiene, viz. isoprene,⁷¹ the most abundant non-methane biogenic hydrocarbon.^{155, 156} Although direct spectroscopic or kinetic measurement of the peroxy radicals in isoprene oxidation has not been reported, their base unit, the allyl peroxy radical was observed via room-temperature cavity ring-down (CRD) spectroscopy.⁷² Using *ab initio* calculated molecular constants, rotational contours of all five conformers of allyl peroxy were generated and

used to simulate experimentally obtained CRD spectrum of the radical. Allyl peroxy is the smallest peroxy radical with the allyl functional group. Its alkyl substitution introduces more isomer and complicates the conformational landscape. Moreover, chemical reactions that produce substituted allyl peroxies involve intermediates that possess multiple resonance structures, which leads to complex reaction kinetics. Here we report room-temperature CRD spectra of the methylallyl peroxy (MAOO $\cdot$) radical. MAOO $\cdot$ has three positional isomers (1-, 2-, and 3-MAOO $\cdot$). Each isomer has multiple rotational conformers or rotamers. Limited by spectral linewidth, transitions of individual conformers were not resolved in the present work. Nevertheless, spectral simulation aided by quantum chemical calculations allows identification of molecular carriers of recorded CRD spectra, which is essential to future kinetic studies. Furthermore, simulating the experimental spectra helps understand chemical reactions that produce the MAOO $\cdot$ radicals and the role of resonance-stabilized free radical intermediates in the process.

8.2 Calculations

The PES of each MAOO $\cdot$ isomer is complicated by the existence of multiple conformations. In this section, we first provide an overview of the PES landscapes and the conformational search. Geometry optimization and energy calculation of both $\tilde{X}$ - and $\tilde{A}$ -state molecules will follow. They provide molecular constants and other quantities that are necessary for spectral simulation, including relative populations of different conformers of each isomer, frequencies, and oscillator strengths of their $\tilde{A} \leftarrow \tilde{X}$ electronic transitions, vibrational frequencies, and Franck-Condon factors (FCFs) of the vibronic transitions.

8.2.1 PES Survey and Conformational Search

The conformational search of the MAOO $\cdot$ radical has been done on the basis of the allyl peroxy ($\text{CH}_2=\text{CHCH}_2\text{OO}\cdot$) radical,⁷² which has two dihedral angles (Φ_1 : OOC_3C_2 and Φ_2 : $\text{OC}_3\text{C}_2=\text{C}_1$). Each dihedral angle can have three orientations in stable conformers: trans (T), counterclockwise gauche (G), and clockwise gauche (G') for Φ_1 ; cis (C), G, and G' for Φ_2 . Among the total $3\times 3=9$ stable conformers, there are four pairs of enantiomers, which belong to the C_1 point group. Therefore, the allyl peroxy radical has five optically distinguishable conformers. For MAOO $\cdot$, we label the carbon atoms the same way would the allyl peroxy radical. The carbon atom in the substituting methyl group is labeled "C_m." (See Figure 8.2)

1-MAOO $\cdot$, a straight-chain molecule, has three dihedral angles: Φ_1 : OOC_3C_2 , Φ_2 : $\text{OC}_3\text{C}_2=\text{C}_1$, and Φ_3 : $\text{C}_3\text{C}_2=\text{C}_1\text{C}_m$. Its conformations are therefore named according to these dihedral angles. Like in the allyl peroxy radical, rotation about a non-CH single bond introduces three conformations. If the rotating bond is a single bond and both adjacent bonds are single bonds too, e.g., Φ_1 , the three possible conformations are T (trans- with $\Phi\sim 180^\circ$), G (gauche with $\Phi\sim 60^\circ$ counterclockwise), and G' (gauche with $\Phi\sim 60^\circ$ clockwise). If the rotating bond is a single bond and one of the adjacent bonds is a double bond, e.g., Φ_2 , the three conformations are: C (cis- with $\Phi\sim 0^\circ$), G (gauche with $\Phi\sim 120^\circ$ counterclockwise), and G' (gauche with $\Phi\sim 120^\circ$ clockwise). Rotation about a C=C double bond, e.g., Φ_3 , introduces two conformations C (cis- with $\Phi\sim 0^\circ$) and T (trans- with $\Phi\sim 180^\circ$). In total, there are $3\times 3\times 2=18$ conformations. Two of these conformations, namely, TCC and TCT, belong to the C_s point group. The rest of the 16 conformations, belonging to the C_1 point group, form eight pairs of enantiomers, which reduces the total

number of optically distinguishable conformations to ten. Geometry optimization showed that GCC (C_1) and one of the C_s conformations, namely, TCC (C_s), are actually transition structures. 1-MAOO $\cdot$, therefore, has eight optically distinguishable stable conformers.

2-MAOO $\cdot$ can be derived from allyl peroxy by methyl substitution at the C_2 position in the parent chain. Because there is only one hydrogen atom connected to C_2 and internal rotation of the methyl group does not introduce new conformations, the number of optically distinguishable conformations of 2-MAOO $\cdot$ is the same as the allyl peroxy radical, i.e., 5. They are named according to the dihedral angles Φ_1 : OOC $_3$ C $_2$ and Φ_2 : OC $_3$ C $_2$ =C $_1$. Geometry optimization shows that all five conformations are stable structures.

Similarly, 3-MAOO $\cdot$ can be viewed as methyl substitution of allyl peroxy, where the methyl group is attached to C_3 . In the allyl peroxy radical, there are two hydrogen atoms connected to C_3 . They are equivalent for the TC (C_s) conformation but distinct for the rest 4 C_1 ones. 3-MAOO $\cdot$, therefore, has $1 \times 1 + 4 \times 2 = 9$ optically distinguishable conformations. The conformations of 3-MAOO $\cdot$ are named again by Φ_1 : OOC $_3$ C $_2$ and Φ_2 : OC $_3$ C $_2$ C $_1$. Since the dioxygen moiety and C_m are at the same center, the third dihedral angle, Φ_3 : C $_m$ C $_3$ C $_2$ C $_1$, is predetermined given a certain combination of Φ_1 and Φ_2 . It hence does not introduce new conformations. All nine conformations are stable structures. Since all 3-MAOO $\cdot$ conformers belong to the C_1 point group, each of them has its enantiomer.

Table 8.1 summarizes the numbers of (optically distinguishable) conformations, transition structures, and stable conformers of all three isomers of MAOO $\cdot$. Newman's projections are illustrated in Figures 8.8-10.

8.2.2 Quantum Chemical Calculations

Density functional theory (DFT) calculations at the B3LYP/6-31+G(d,p) level of theory were carried out on ground-state MAOO $\cdot$ conformers using the Gaussian 09 software package.¹¹⁴ Relative energies of conformers with zero-point energy corrections are listed in Tables 8.2 and 8.3. Time-dependent (TD-)DFT calculations at the same level were employed for calculations of $\tilde{A}$ -state molecules. Geometries and vibrational frequencies of both states were predicted in the calculations. In addition, vertical and adiabatic excitation energies of the $\tilde{A} \leftarrow \tilde{X}$ transition were determined. The calculated geometric parameters of all conformers are summarized in Table 8.4.

8.2.3 Spin Densities of the 1-MA Radical and PES Scan Along the Reaction Coordinate of Oxygen Addition

The 1-MA radical has two resonance structures ($\text{CH}_3\text{CH}=\text{CHCH}_2\cdot$ and $\text{CH}_3\text{CH}\cdot\text{CH}=\text{CH}_2$). Their population ratio at equilibrium is determined by the nature and extent of electron delocalization. Atomic partition of the spin density at the B3LYP/6-31+G(d,p) level of theory¹⁵⁷ finds that 52% of the spin is on the terminal C and 48% on the non-terminal one (Figure 8.3).

In order to compare reaction rate constants $k_{1\text{-MAOO}}$ and $k_{3\text{-MAOO}}$, the Complete Basis Set (CBS)-QB3 method was employed to scan the PESs along the reaction coordinate of oxygen addition. In these calculations, the distance between the C₃ atom and the center of the OO moiety is varied from 1.5 Å to 6.0 Å. Other coordinates are optimized at each step of the PES scan. Since the gauche conformer of the 1-MA radical is significantly lower in

energy than its cis conformer, only the lowest-energy conformers of 1- and 3-MAOO $\cdot$ with a gauche CCCC dihedral angle are included. The scans of PESs along the reaction coordinates are plotted in Figure 8.4. Oxygen addition on either the terminal or the non-terminal positions has a small barrier (<3 kcal/mol) because of the elimination of the allylic resonance.¹⁵⁸ Both the heights of the barriers and the depth of the wells are similar for the production of 1- and 3-MAOO $\cdot$ s. Reaction rate constants $k_{1\text{-MAOO}}$ and $k_{3\text{-MAOO}}$, are therefore expected to be close.

Because the two free radical positions of 1-MA have similar spin densities and the reaction rates for oxygen addition on these two positions are expected to be similar, the branching ratio between production of 1- and 3-MAOO $\cdot$'s using either 1-chloro-2-butene or 3-chloro-1-butene as a precursor (Reactions 5 and 6) is expected to be 1:1.

8.3 Spectral Simulation and Assignment

Calculated adiabatic $\tilde{A} \leftarrow \tilde{X}$ transition frequencies of MAOO $\cdot$ conformers are used to simulate experimentally observed spectra. Calculation of transition intensities takes into consideration the following factors:

8.3.1 Relative Populations of MAOO $\cdot$ Isomers

When 3-chloro-2-methyl-1-propene is used as the precursor, only one of the three isomers of MAOO $\cdot$, namely, 2-MAOO $\cdot$, can be produced. Its relative population is therefore set to unity. Both 1- and 3-MAOO $\cdot$ isomers can be produced using either 1-chloro-2-butene or 3-chloro-1-butene as a precursor. Based on the discussion above, populations of these two

isomers are expected to be close. In the spectral simulation, weights of these two isomers are set to 52:48, the ratio of spin densities on the terminal and non-terminal positions of the 1-MA radical.

8.3.2 Population Ratios of Different Conformers of Each Isomer

PES scans, along with reaction coordinates that connect different rotamers of each isomer of MAOO $\cdot$, are illustrated in Figures 8.11-16. The energy barriers are relatively low (<3 kcal/mol). In the spectra simulation, we assumed that relative populations of all conformers of each isomer follow the Boltzmann distribution. The Boltzmann distribution factors and relative populations of conformers are given in Tables 8.2 and 8.3. As shall be demonstrated below, the assumption of the Boltzmann distribution does not always provide the ideal simulation of transition intensities.

8.3.3 Degeneracy of Each Conformer

This is equal to the number of enantiomers of each conformer. Conformers that belong to the C_s point group have a single conformation. For other conformers, belonging to the C_1 point group, there are two equivalent conformations that are not optically distinguishable. The weights for the latter conformers are therefore doubled in spectral simulation. The degrees of the degeneracy of MAOO $\cdot$ conformers are given in Tables 8.2 and 8.3.

8.3.4 Oscillator Strength of the Electronic Transition for each Conformer

$\tilde{A} \leftarrow \tilde{X}$ transition of peroxy radicals is analogous to the triply forbidden $a^1\Delta_g - \tilde{X}^3\Sigma_g^-$ transition of O_2 . Due to the nature of the forbidden transition, TD-DFT calculated oscillator strengths are not reliable. Because the electron promotion is localized to the OO moiety and the influence of the molecular conformation is expected to be insignificant, oscillator strengths of different conformers of MAOO $\cdot$ are all set to unity in the spectral simulation.

8.3.5 Franck-Condon Factors (FCFs) of the Vibronic Transitions

FCFs for vibronic transitions were calculated using the ezSpectrum program.¹²¹ Because the electron promotion is limited to the dioxygen moiety, the most significant geometric change for the $\tilde{A} \leftarrow \tilde{X}$ transition is the elongation of the OO bond (see Table 8.4). Therefore, only the origin ($v' = 0$ to $v'' = 0$) transitions and transitions to $\tilde{A}$ -state vibrational levels with OO-stretch characters have considerable FCFs, as confirmed by calculations using ezSpectrum.

Relative transition intensities of all conformers are calculated as products of the factors listed above. To simulate the experimental spectra, several line-broadening mechanisms need to be considered, including the linewidth of the light source (~ 1 GHz), Doppler broadening (300 MHz), and pressure broadening (on the order of 1 GHz under the current experimental conditions). With these line-broadenings, the rotational structure of MAOO $\cdot$ radicals cannot be resolved, and only rotational contours are expected in the experimental spectra. However, these mechanisms are not sufficient to explain the absence of any narrow features in the experimental spectra attributable to MAOO $\cdot$ (see below). The lack of narrow features in the experimental CRD spectra can be explained by lifetime

broadening, which was detected in previous CRD spectra of the allyl peroxy radical.⁷² Due to the weak CO bond, the $\tilde{A}$ state of allyl peroxy is expected to overlap with the dissociative continuum of the $\tilde{X}$ state, which leads to predissociation and short lifetime of $\tilde{A}$ -state energy levels. Spectral simulation using an asymmetric rotor model suggests that lifetime broadening on the order of 1 cm^{-1} would remove remaining features in the rotational contours of MAOO $\cdot$, which span more than 10 cm^{-1} . Therefore, instead of adopting simulated rotational contours, calculated transition intensities are convoluted by a Gaussian line shape with a full width at half maximum (FWHM) of 15 cm^{-1} in the present work. Simulated spectra of all produced conformers are superposed to reproduce the room-temperature CRD spectra.

8.3.6 Simulation of CRD Spectrum of 2-MAOO $\cdot$

We first compare the experimental and simulated spectra of 2-MAOO $\cdot$ (Figure 8.5) as it was separated from the other two isomers in free radical production. The lowest-frequency and strongest peak at $\sim 7640\text{ cm}^{-1}$ in the experimental spectrum is assigned to the $\tilde{A} \leftarrow \tilde{X}$ origin. However, TD-DFT calculations overestimate the electronic transition frequencies. A scaling factor of 0.887 is therefore applied to calculated electronic transition frequencies of all conformers to match the experimental and simulated spectra. Simulated spectra of all conformers of 2-MAOO $\cdot$ are weighted by their calculated relative populations and combined to generate the overall spectrum of 2-MAOO $\cdot$ (thick line in Figure 8.5b). (See Figure 8.17). The simulation underestimates the transition intensity of the lowest-energy conformer (TG). Such discrepancy between the experimental and simulated intensities may be attributed to inaccuracy in the calculation of FCFs and/or to the non-Boltzmann

distribution of different conformers. Figure 8.6 compares the experimental spectrum to simulations assuming Boltzmann distribution at different temperatures. Simulation with $T=50$ K best reproduces the experimental spectrum.

The spectral simulation predicts a strong transition to the $\nu = 1$ level of the OO stretch mode. Experimentally, a strong peak $\sim 8615\text{ cm}^{-1}$ blue-shifted from the origin band was observed in the CRD spectrum and can be assigned to the OO-stretch band. The calculated $\tilde{A}$ -state OO-stretch frequencies of 2-MAOO $\cdot$ conformers are listed in Table 8.3. To better reproduce the experimental spectrum, a scaling factor of 0.9 is applied to the calculated vibrational frequencies. It should be compared to the scaling factor of 0.964 ± 0.023 recommended by the CCCDBD database¹⁰⁷ for B3LYP/6-31+G(d,p) calculations, which implies that TD-DFT calculations used in the present work significantly overestimate the $\tilde{A}$ state OO bond strength.

8.3.7 Simulation of CRD Spectra of 1-MAOO $\cdot$ and 3-MAOO $\cdot$

CRD spectra of 1- and 3-MAOO $\cdot$ using 3-chloro-1-butene or 1-chloro-2-butene as a precursor are shown in Figure 8.7a and 8.7b, respectively. These two spectra using different precursors are almost identical, which confirms the expectation that allylic rearrangement is significantly faster than oxygen addition. Strong absorption with sharp features between 7300 and 7500 cm^{-1} is due to methyl peroxy.¹⁵⁹ In addition, a broad and long-lived baseline absorption is present in both spectra. It is attributed to unidentified stable photolysis products.

Simulated spectra of all conformers of each isomer are combined to generate spectra of the isomers (thick lines in Figure 8.7c and 8.7d) (See Figures 8.18 and 8.19 for details.) By matching the calculated $\tilde{A} \leftarrow \tilde{X}$ adiabatic transition frequencies to the strong origin bands in the experimental spectra at 7610 cm^{-1} (1-MAOO $\cdot$) and 7810 cm^{-1} (3-MAOO $\cdot$), electronic scaling factors are determined to be 0.879 and 0.887 for 1- and 3-MAOO $\cdot$, respectively. The OO-stretch region of the experimental spectra is contaminated by strong precursor absorption (See Figure 8.20). Therefore, OO-stretch bands of 1- and 3-MAOO $\cdot$ were not observed. Nevertheless, the same vibrational scaling factor as 2-MAOO $\cdot$ (0.9) is used in the simulation of the spectrum of 1- and 3-MAOO $\cdot$ radicals.

In simulating the overall spectra of 1- and 3-MAOO $\cdot$ isomers (Figure 8.7e), the relative populations of 1-MAOO $\cdot$:3-MAOO $\cdot$ is set to 52:48, the calculated ratio of spin densities on the terminal and non-terminal positions. The simulated spectrum reproduces the experimental one qualitatively. In Figure 8.21, the population ratio is adjusted to demonstrate its effect on the overall spectrum. Although an accurate determination of the population ratio from the experimental spectrum is not possible due to the existence of the broad baseline and interference of the CH₃OO $\cdot$ absorption, the experimental CRD spectrum confirms that populations of the 1- and 3-MAOO $\cdot$ radicals produced in the present experiment are comparable to each other.

8.4 Conclusions

Room-temperature CRD spectra of $\tilde{A} \leftarrow \tilde{X}$ electronic transitions of all three isomers of the MAOO $\cdot$ radical have been recorded. The free radicals were produced in a 193 nm photolysis of selected methyl-substituted allyl chlorides, including 1-chloro-2-butene, 3-

chloro-2-methyl-1 propene, and 3-chloro-1-butene, in the presence of O₂. The vibronic structure of experimentally observed spectra was simulated using calculated electronic transition frequencies, vibrational frequencies, and FCFs. When 1-chloro-2-butene or 3-chloro-1-butene is used as a precursor, either of the two resonance-stabilized structures of 1-MA ($\text{CH}_3\text{CH}=\text{CHCH}_2\cdot \leftrightarrow \text{CH}_3\text{CH}\cdot\text{CH}=\text{CH}_2$) is produced in the photolysis. The subsequent allylic rearrangement and interconversion between the two resonance structures are significantly faster than oxygen addition that forms the peroxy radicals, resulting in identical peroxy spectra using these two precursors. Spin density calculations and PES scans suggest that the branching ratio between the terminal and non-terminal oxygen addition is close to unity, which is confirmed in simulating the overall spectra of 1- and 3-MAOO[•] radicals.

The experimental investigation reported in the present paper is the first attempt at the spectrum of an important and intriguing free radical. In order to reduce spectral congestion and achieve better resolution, one may produce the MAOO[•] radicals with the pulsed discharge of stable precursors in a slit-jet supersonic expansion in the presence of oxygen.^{104, 160} Also, it would be beneficial to use narrow linewidth near-IR sources, e.g., the first-order Stokes of a Ti:Sapphire amplifier.¹⁶¹ Construction of a high-resolution, jet-cooled CRD spectroscopy apparatus is in process.

Table 8.1. Numbers of (optically distinguishable) conformations, transition structures, and stable conformers of 1-, 2- and 3-MAOO[•] radicals.

isomer	conformations			optically distinguishable conformations	transition structures	stable conformers
	C_s	C_1	total			
1-MAOO [•]	2	16	18	10	2	8
2-MAOO [•]	1	8	9	5	0	5
3-MAOO [•]	0	18	18	9	0	9

Table 8.2. Relative energies, Boltzmann distribution factors, and relative populations of 1- and 3-MAOO[•] conformers. $\Delta E^{\tilde{A}-\tilde{X}}$ is the adiabatic transition frequency between the $\tilde{X}$ and $\tilde{A}$ states. $\nu_{\text{OO}}(\tilde{A})$ is the $\tilde{A}$ -state OO stretch frequency.

isomer	conformer	no. of enantiomers	relative energy ^a (cm ⁻¹)	Boltzmann distribution factor ^b	relative population ^c (%)	$\Delta E^{\tilde{A}-\tilde{X}}$ (cm ⁻¹)	$\nu_{\text{OO}}(\tilde{A})$ (cm ⁻¹)
1-MAOO [•]	TGT	2	0	0.41	21.4	7607	1012
	GGT	2	60	0.31	16.0	7671	1013
	GG'T	2	138	0.21	11.0	7594	1004
	TCT	1	598	0.01	0.6	7517	1043
	GCT	2	658	0.02	0.9	7555	1002
	TGC	2	669	0.02	0.8	7605	1011
	GGC	2	724	0.01	0.6	7782	1014
	GG'C	2	787	0.01	0.5	7646	1008
	GCC ^d	2					
	TCC ^d	1					
3-MAOO [•]	TG'	2	182	0.32	15.1	7801	1012
	GG'	2	200	0.29	13.8	7766	1012
	G'G'	2	372	0.13	6.1	7840	1006
	GG	2	469	0.08	3.8	7876	1023
	TG	2	477	0.08	3.7	7817	1014
	TC	2	566	0.05	2.4	7723	1036
	GC	2	604	0.04	2.0	7596	1022
	G'G	2	810	0.02	0.7	7715	994
	G'C	2	943	0.01	0.4	7635	999

^a Zero-point energy corrections included.

^b Normalized for each isomer.

^c Normalized for 1- and 3-MAOO[•] combined. The population ratio of 1-MAOO[•]:3-MAOO[•] is set to 52:48. (See text).

^d Transition structures.

Table 8.3. Relative energies, Boltzmann distribution factors, and relative populations of 2-MAOO' conformers. $\Delta E^{\tilde{A}-\tilde{X}}$ is the adiabatic transition frequency between the $\tilde{X}$ and $\tilde{A}$ states. $\nu_{\text{OO}}(\tilde{A})$ is the $\tilde{A}$ -state OO stretch frequency.

isomer	conformer	no. of enantiomer	relative energy ^a (cm ⁻¹)	Boltzmann distribution factor ^b	relative population ^b (%)	$\Delta E^{\tilde{A}-\tilde{X}}$ (cm ⁻¹)	ν_{OO} (cm ⁻¹)
2-MAOO'	TG	2	0	0.37	37.5	7642	1023
	GG	2	52	0.29	29.3	7812	1014
	G'G	2	98	0.23	23.4	7534	1002
	TC	1	350	0.07	7.0	7596	1046
	GC	2	388	0.03	2.9	7657	1034

^a Zero-point energy corrections included.

^b Normalized.

Table 8.4. Geometric parameters of conformers of 1-, 2- and 3- MAOO[•] radicals in the $\tilde{X}$ and $\tilde{A}$ states calculated at the B3LYP/6-31+G(d,p) level of theory.

isomer	conformer	geometric parameter									
		O-O (Å)		$\angle$ OOC (deg.)		ϕ OOCC (deg.)		ϕ OCCC (deg.)		ϕ CCCC (deg.)	
		$\tilde{X}$	$\tilde{A}$	$\tilde{X}$	$\tilde{A}$	$\tilde{X}$	$\tilde{A}$	$\tilde{X}$	$\tilde{A}$	$\tilde{X}$	$\tilde{A}$
1-MAOO [•]	TGT	1.32	1.38	111	108	169	174	114	114	179	178
	GGT	1.32	1.38	112	109	82	72	116	114	180	178
	GG'T	1.32	1.38	112	110	77	70	-114	-124	-180	-179
	TCT	1.32	1.38	111	108	180	180	0	0	180	180
	GCT	1.33	1.38	112	110	89	71	-8	0	180	180
	TGC	1.32	1.38	111	108	-172	-175	-113	-112	0	1
	GGC	1.32	1.38	112	109	80	70	119	116	0	-1
	GG'C	1.32	1.38	112	110	78	71	-112	-125	0	2
	TCC ^a	1.32	1.38	111	108	180	180	0	0	0	0
	GCC ^{a,b}										
2-MAOO [•]	TG	1.32	1.38	112	108	168	176	117	121		
	GG	1.32	1.38	112	111	95	75	114	109		
	G'G	1.32	1.38	112	110	-79	-67	120	131		
	TC	1.32	1.38	111	108	180	180	0	0		
	GC	1.33	1.39	112	110	90	74	-5	1		
3-MAOO [•]	TG'	1.32	1.38	112	110	167	175	-118	-119		
	GG'	1.32	1.38	112	110	77	66	-116	-125		
	G'G'	1.32	1.38	113	112	-65	-68	-118	-117		
	GG	1.32	1.38	112	110	74	70	130	133		
	TG	1.32	1.38	112	110	158	164	129	129		
	TC	1.32	1.38	112	109	160	168	-2	-2		
	GC	1.32	1.38	112	111	88	70	-3	6		
	G'G	1.32	1.38	112	111	-65	-66	134	139		
	G'C	1.32	1.38	113	113	-77	-70	6	2		

^a Transition structures.

^b Converges to the GGC conformer upon geometry optimization.

Figure 8.1. Schematics of production of (a) 2-MAOO $\cdot$ radical using 3-chloro-2-methyl-1-propene as the precursor, and 1- and 3-MAOO $\cdot$ radicals using either (b) 1-chloro-2-butene or (c) 3-chloro-1-butene as the precursor. Bidirectional arrows denote allylic rearrangement.

Figure 8.2. Schematics of 1-, 2- and 3-MAOO[•] radicals showing the convention used to label carbon atoms in the present work.

Figure 8.3. Plots of spin densities of $\tilde{X}$ -state (a) *cis*-1-methylallyl and (b) *trans*-1-methylallyl radicals calculated at the B3LYP/6-31+(d,p) level of theory. The regions in red and purple meshes represent excess α spin and β spin, respectively.

Figure 8.4. PES scans for production of 1- and 3-MAOO $\cdot$ isomers along the reaction coordinate of oxygen addition. $R_{C...OO}$ is the distance between the C $_3$ atom and the center of mass of the OO moiety.

Figure 8.5. (a) Experimental CRD spectrum of the 2-MAOO· radical (red) in comparison with simulation at the temperature of 300 K (green). Sharp peaks between 7300 and 7500 cm^{-1} in the experimental spectrum are due to residual water absorption. (b) Simulated spectrum of 2-MAOO·. Thin lines are simulated spectra of individual conformers weighted by relative populations. The thick green line is superposition of simulated spectra of all conformers.

Figure 8.6. (a) Experimental CRD spectrum of the 2-MAOO[•] radical (red) in comparison with simulation at the temperature of 50 K (purple). (b) Simulated spectra of 2-MAOO[•] at different temperatures. Overall spectra of 2-MAOO[•] are calculated as summation of spectra of all conformers weighted by their relative populations assuming the Boltzmann distribution (not shown in the figure). All spectra are offset for clarity. The simulation with T=50 K (purple) reproduces the experimental spectrum the best.

Figure 8.7. CRD spectrum of the 1- MAOO $\cdot$ and 3- MAOO $\cdot$ radicals using either (a) 3-chloro-1-butene (blue) or (b) 75% 1-chloro-2-butene and 25% 3-chloro-1-butene mixture (red) as precursors. Strong absorption with sharp features between 7300 and 7500 cm^{-1} is due to methyl peroxy. Experimental spectra are compared with simulated overall spectra of 1- and 3-MAOO $\cdot$ radicals (green). (c) Simulated spectrum of 1-MAOO $\cdot$. (d) Simulated spectrum of 3-MAOO $\cdot$. Thin lines in (c) and (d) are simulated spectra of individual conformers weighted by populations, while the thick green line is their superposition. (e) Superposition of the simulated spectra of both isomers (green) with weights of 52% for 1-MAOO $\cdot$ (red) and 48% for 3-MAOO $\cdot$ (blue).

Figure 8.8. Newman projections of 1-MAOO' conformers.

Figure 8.9. Newman projections of 2-MAOO' conformers.

Figure 8.10. Newman projections of 3-MAOO' conformers.

Figure 8.11. A scan of the potential energy surface of 1-MAOO' along the coordinate of the CCOO dihedral angle. Molecular geometry is optimized at each step of the scan.

Figure 8.12. A scan of the potential energy surface of T 1-MAOO' along the coordinate of the CCOO dihedral angle. Molecular geometry is optimized at each step of the scan.

Figure 8.13. A scan of the potential energy surface of 2-MAOO' along the coordinate of the CCOO dihedral angle. Molecular geometry is optimized at each step of the scan.

Figure 8.14 A scan of the potential energy surface of 2-MAOO along the coordinate of the CCCO dihedral angle. Molecular geometry is optimized at each step of the scan.

Figure 8.15. A scan of the potential energy surface of 3-MAOO' along the coordinate of the CCOO dihedral angle. Molecular geometry is optimized at each step of the scan.

Figure 8.16. A scan of the potential energy surface of 3-MAOO along the coordinate of the CCCO dihedral angle. Molecular geometry is optimized at each step of the scan.

Figure 8.17. Simulated spectra of 2-MAOO conformers. Overall spectrum of 2-MAOO is calculated as summation of spectra of all conformers weighted by their relative populations at 300 K. All spectra are offset for clarity.

Figure 8.18. Simulated spectra of 1-MAOO conformers. Overall spectrum of 2-MAOO is calculated as summation of spectra of all conformers weighted by their relative populations at 300 K. All spectra are offset for clarity.

Figure 8.19. Simulated spectra of 3-MAOO' conformers. Overall spectrum of 3-MAOO' is calculated as summation of spectra of all conformers weighted by their relative populations at 300 K. All spectra are offset for clarity.

Figure 8.20. CRD spectra of MAOO' isomers (red) and their precursors: 3-chloro-2-methyl-1-propene for 2-MAOO' production (*top*), and 75% 1-chloro-2-butene and 25% 3-chloro-1-butene mixture for 1- and 3-MAOO' production (*bottom*). The free radical spectra are obtained by subtracting the “photolysis laser off” spectrum (black) from the “photolysis laser on” spectrum (blue).

Figure 8.21. (a) CRD spectrum of the 1- MAOO[•] and 3-MAOO[•] radicals. (b) Simulated spectrum of 52% 1-MAOO[•] + 48% 3-MAOO[•] (c) Simulated spectra with different population ratios of 1- MAOO[•] and 3- MAOO[•]. Spectra are offset for clarity.

CHAPTER IX

CONCLUSIONS

Alkoxy and peroxy radicals are important reaction intermediates in the combustion of fossil fuels and the atmosphere, especially in the troposphere. Spectroscopic study of the free radicals, namely substituted and unsaturated alkoxy and peroxy radicals can advance our understanding of many important chemical processes, including the combustion of fossil fuels and biofuels in internal combustion engines, and oxidation of hydrocarbons in the atmosphere. Spectroscopic characterization of these intermediates can provide information on their structural as well as dynamical properties. Spectroscopy of these intermediates can also help understand interesting molecular phenomena like the pseudo-Jahn Teller effect (pJT).

LIF, DF, and CRDS techniques have been implemented to study reactive chemical intermediates. Spectra of isobutoxy, 2-methyl-1-butoxy, isopentoxy, 1-, 2-, 3-, and 4-MCHO and methyl allyl peroxy radicals were obtained, analyzed and assigned on the basis of vibrational frequencies and Franck-Condon factors predicted by quantum chemical calculations. These calculations provided useful spectroscopic parameters such as rotational constants, harmonic and anharmonic vibrational frequencies, electronic excitation energies, and intensities of vibronic transitions.

LIF spectrum of isopentoxyl and DF spectra of isobutoxy, 2-methyl-1-butoxy, isopentoxyl, and MCHO radicals were obtained, and the single-conformer assignments have been confirmed by pumping different vibronic bands in their LIF spectrum. Different vibrational structures have been observed in the DF spectra when different vibronic bands in the LIF spectrum of each radical were pumped, which suggests that those vibronic bands be assigned to different conformers. In general, spectral simulation confirms lowest-energy conformers as spectral carriers. Analysis of the spectra yields the energy separation between the vibrationless levels of the $\tilde{X}$ and $\tilde{A}$ states for most of the isomers and conformers. Both LIF and DF spectra of alkoxy radicals are usually dominated by CO-stretch progressions because of the large difference in CO-bond length between the ground ($\tilde{X}$) and the excited ($\tilde{B}$) electronic states, hence the large FC factors for the transitions. However, in the case of isopentoxyl radicals, $\tilde{B}$ -state β C-C fission or predissociation of the $\tilde{B}$ state via CO-bond breaking by highly excited electronic states may cause an absence of strong transitions to the CO-stretch levels. When non-CO stretch bands are pumped, the DF spectra are dominated by progressions of combination bands of the CO stretch and the pumped modes as a result of Duschinsky mixing.

Furthermore, LIF and DF spectra often contain transitions that gain intensities from vibronic interactions. For instance, in LIF spectra of branched alkoxy radicals, such as isopentoxyl, we observed low-frequency vibrational progressions that are assigned to the pJT-active CH₂O-wagging mode. In all cases, (except 1-MCHO), the DF spectra are dominated by CO stretch progressions when the origin bands are pumped and by the progression of combination bands of CO stretch and the pumped modes when other non-CO stretch bands are pumped. Simulated spectra using calculated vibrational frequencies

and FCFs well reproduced the DF spectra. The observed transitions were assigned on the basis of vibrational frequencies and FCFs predicted by quantum chemical calculations. Intensities of vibronic transitions in the DF spectra are dependent on the LIF bands pumped in the experiment, which have been explained by the difference in geometry and symmetry between the lower $\tilde{X} / \tilde{A}$ states and the highly excited $\tilde{B}$ state. Differences between DF spectra obtained by pumping different vibronic bands also suggest that for these free radicals have at least two lowest-energy conformers generated by 355 nm photolysis under jet-cooled conditions. Intensities of vibronic transitions in the DF spectra are dependent on the LIF bands pumped in the experiment, which have been explained by the difference in geometry and symmetry between the lower $\tilde{X} / \tilde{A}$ states and the highly excited $\tilde{B}$ state. Detailed spectral analysis of MCHOs enhance the understanding of vibronic interaction mechanisms such as (pJT) effect.

DF spectra of 1-MCHO are significantly different from those of the other three positional isomers. Both chair-axial and chair-equatorial conformers of 1-MCHO has strong progressions that involve both CO stretch and C-CH₃ stretch modes. Such difference is due to different positions of the methyl group on the six-membered ring and the steric interaction between the CO bond and the methyl group of 1-MCHO.

We produced 1-, 2- and 3-methylallyl peroxy (MAOO[•]) radicals by 193 nm photolysis of methyl-substituted allyl chlorides in the presence of O₂ and detected them using room-temperature CRD spectroscopy. The vibronic structure of experimentally observed spectra was simulated. The reaction intermediates for the production of 1- and 3-MAOO[•] radicals, CH₃CHCHCH₂, is a resonance-stabilized free radical. CRD spectra of 1- and 3-MAOO[•] radicals obtained using different precursors (1-chloro-2-butene and chloro-

1-butene) suggest that allylic rearrangement between the two resonance structures ($\text{CH}_3\text{CH}=\text{CHCH}_2\cdot$ and $\text{CH}_3\text{CH}\cdot\text{CH}=\text{CH}_2$) is significantly faster than oxygen addition. The branching ratio between the terminal and non-terminal oxygen addition to forming 1- and 3-MAOO $\cdot$, respectively, were predicted to be 52:48 on the basis of calculated spin densities, which agrees qualitatively with the experimental CRD spectra of the two peroxy isomers.

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Dispersed Fluorescence Spectroscopy of Jet-Cooled Isobutoxy and 2-Methyl-1-butoxy Radicals

Author: Md. Asmaul Reza, Anam C. Paul, Neil J. Reilly, et al

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Laser-Induced Fluorescence and Dispersed Fluorescence Spectroscopy of Jet-Cooled Isopentoxy Radicals

Author: Md Asmaul Reza, Anam C. Paul, Neil J. Reilly, et al

Publication: The Journal of Physical Chemistry A

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Dispersed Fluorescence Spectroscopy of Jet-Cooled 2-, 3-, and 4-Methylcyclohexoxy Radicals

Author: Jahangir Alam, Md. Asmaul Reza, Amy Mason, et al

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Room-Temperature Cavity Ring-Down Spectroscopy of Methylallyl Peroxy Radicals

Author: Md Asmaul Reza, Hamzeh Telfah, Raobo Xu, et al

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PUBLICATIONS

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9. Koncz, B., Bazsó, G., **Reza, M. A.**, Telfah, H., Hegedüs, K., Liu, J.; Tarczaya, G.,
Revealing Long-Range Substituent Effects in the Laser-Induced Fluorescence and
Dispersed Fluorescence Spectra of Jet-cooled $\text{CH}_x\text{F}_3-x\text{CH}_2\text{O}$ ($x=1,2,3$) Radicals. *J. Phys. Chem. A* (submitted).
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Dispersed Fluorescence Spectroscopy of Jet-Cooled Isopentoxy Radicals. *J. Phys. Chem. A*, **2019**, 123, 39, 8441-8447.
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Fluorescence and Dispersed Fluorescence Spectroscopy of the $\tilde{A}^2\text{E} \leftarrow \tilde{X}^2\text{A}_1$ Transition of
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CONFERENCE PRESENTATIONS

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7. **Md Asmaul Reza**, Hamzeh Telfah, Anam C. Paul, Jahangir Alam, Jinjun Liu. Cavity Ring-down Spectroscopy of 1-, 2- and 3-methylallyl peroxy radicals. *73rd International Symposium on Molecular Spectroscopy, Champaign-Urbana, Illinois, USA.* June 2018
 6. Hamzeh Telfah, **Md Asmaul Reza**, Anam C. Paul, Jinjun Liu. Observation of The $\tilde{A} \leftarrow \tilde{X}$ Electronic Transitions of Tetrahydropyranyl and Tetrahydrofuranyl Peroxy Radicals by Room-Temperature Cavity Ring-Down Spectroscopy. *73rd International Symposium on Molecular Spectroscopy Champaign-Urbana, Illinois, USA.* June 2018
 5. Anam C. Paul, **Md Asmaul Reza**, Ketan Sharma, Terry A. Miller, Jinjun Liu, Alkaline Earth Monoalkoxide Free Radicals as Candidates for Laser Cooling of Poly-Atomic Molecules. *73rd International Symposium on Molecular Spectroscopy, Champaign-Urbana, Illinois, USA.* June 2018

4. Anam C. Paul, **Md Asmaul Reza**, Pranoy Deb Shuvra, Jinjun Liu. Laser-Induced Fluorescence and Dispersed-Fluorescence Spectroscopy of Jet-Cooled Calcium Monoalkoxide Radicals. *73rd International Symposium on Molecular Spectroscopy, Champaign-Urbana, Illinois, USA*. June 2018
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2. **Md Asmaul Reza**, Neil J Reilly, Jahangir Alam, Amy Mason, Jinjun Liu. Dispersed Fluorescence Spectroscopy of Jet-Cooled Isobutoxy, 2-Methyl-1-butoxy and Isopentoxy Radicals. *69th International Symposium on Molecular Spectroscopy, Champaign-Urbana, Illinois, USA* June 2015
1. Jahangir Alam, **Md Asmaul Reza**, Amy Mason, Jinjun Liu. Dispersed Fluorescence Spectroscopy of Jet-Cooled Methylcyclohexoxy Radicals. *69th International Symposium on Molecular Spectroscopy, Champaign-Urbana, Illinois, USA*. June 2015